PB81-208977

Effects of Sulfuric Acid Mist Exposure on Pulmonary Function

California Univ.
Santa Barbara

Prepared for

Health Effects Research Lab.
Research Triangle Park, NC

Jun 81

U.S. Department of Commerce
National Technical Information Service
NTIS.

PB81-208977

EPA 600/1-81-044
June 1981

EFFECTS OF SULFURIC ACID MIST EXPOSURE ON PULMONARY FUNCTION

by

Steven M. Horvath, Lawrence J. Folinsbee,
and
John F. Bedi

Institute of Environmental Stress
University of California, Santa Barbara
Santa Barbara, California 93106

EPA Grant R804853

Project Officer

Donald H. Horstman

Human Studies Division
Health Effects Research Laboratory
Research Triangle Park, North Carolina 27711

HEALTH EFFECTS RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

PRODUCT OF:
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/1-81-044	ORD Report	

4. TITLE AND SUBTITLE	5. REPORT DATE
Effect of sulfuric acid mist exposure on pulmonary function	June 1981
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
S. Horvath L. Folinsbee I. Bedi	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Institute of Environmental Stress University of California Santa Barbara, CA 93106	C9AN1B
	11. CONTRACT/GRANT NO. R804853

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Project Officer: Donald Horstman MD-58 EPA: Health Effects Research Laboratory Research Triangle Park, NC 27711	Final (4/1/77-8/31/80)
	14. SPONSORING AGENCY CODE EPA-600/11

15. SUPPLEMENTARY NOTES

Project Officer: Donald H. Horstman

16. ABSTRACT

Effects of 2-hr exposure to sulfuric acid (H_2SO_4) on pulmonary functions in male nonsmokers were examined. Subjects were exposed to air and 233, 418 and 939 micrograms/m^3 H_2SO_4 at 22°C DB/55% RH or air and 314, 600 and 1107 micrograms/m^3 H_2SO_4 at 35°C DB/85% RH. Mass median diameter was 0.92 micrometer, a sequence of 20-min exercise (V_E of 30 l/min) and 20-min rest was repeated three times during each exposure. Pulmonary functions (forced vital capacity, lung volumes, maximum voluntary ventilation, airway resistance, total gas volume) were measured pre- and post exposure. In addition, forced vital capacity was determined following each exercise period. No significant changes in pulmonary functions were observed for H_2SO_4 exposure. An increased prevalence of symptoms, such as cough, dry throat or throat irritation, was observed for H_2SO_4 exposure, suggesting that H_2SO_4 may have caused some pulmonary irritation though not sufficient to induce functional changes. It was concluded that 2-hr exposure, with intermittant exercise, to H_2SO_4 in the one micrometer size range and in concentrations up to 1100 micrograms/m^3 had relatively minor effects on the pulmonary system.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Sulfuric Acid Pulmonary Function		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
UNLIMITED	UNCLASSIFIED	90
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

DISCLAIMER

The report has been reviewed by the U. S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTION HERE

FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The Health Effects Research Laboratory, Research Triangle Park, conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides as well as other chemical pollutants. The Laboratory participates in the development and revision of air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is primarily responsible for providing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endangerment of their health.

Considerable interest was and continues to be present in the potential effects that exposure to sulfuric acid mist would have on the cardiopulmonary functions of exposed humans. The present study provides information on responses to a brief exposure to sulfuric acid and in two ambient environments. Young male subjects were exposed for two hours while performing intermittent exercise to sulfate concentrations up to 1400 ug/m^3 with particle size MMD, 0.9 um. Additional studies with sulfuric acid particles of approximately MMD, 0.1 um are nearly completed. These studies will provide information under controlled conditions on the responses of young males but leave unanswered whether or not frmales or older individuals have similar responses. Futhermore, the questions as to what potential synergistic effects would be observed in a multiple-polluted environment remain to be evaluated.

F.G. Hueter, Ph.D
Director,

Health Effects Research Laboratory

BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Orig.) (4-76)

ABSTRACT

The effects of sulfuric acid particle concentration (mass/volume), particle size, and ambient temperatures on pulmonary function of young male nonsmokers were examined. Subjects repeated three times a sequence of 20 min exercise (ventilation of approximately 30 ℓ/min) and 20 min sitting rest. Pre- and post-exposure pulmonary functions (forced vital capacity maneuvers, lung volumes, maximum voluntary ventilation, R_{aw} TGV and helium-oxygen FVC) were measured. During the exposure and at the 5th min after cessation of each exercise period, forced vital capacity tests (air and helium-oxygen) were performed. Each subject was exposed in random order to filtered air or 233, 418 or 939 $\mu g/m^3$ particulate sulfuric acid. Particle sizes were MMD, 0.91-0.93 μm, geometric SD, 1.66-1.73. Two subject groups were studied in two different ambient conditions, i.e. approximately 22°C dry bulb, 55% relative humidity, and 35°C dry bulb, 85% relative humidity. Sulfuric acid concentrations were slightly higher during the hot environmental exposures. No significant changes in pulmonary functions related to sulfate were observed in subjects intermittently exercising in the cool environment. Metabolic measurements during exercise indicated a trend towards increased ventilation and oxygen uptake with duration of exposure. The only significant difference which was related to sulfate exposure was a higher respiratory rate compared to filtered air. Heart rates were similar under all conditions. In the hot humid environment, forced vital capacity decreased with time of exposure but was not related to pollutant exposure. The only significant interaction for pollutants across time was seen for FEF75%, where the post-exposure values were greater than the pre-exposure values under filtered air conditions but not during sulfate exposure. This observation was not corroborated by changes in FEF75-85%, which increased post-exposure under all conditions. Three subjects were studied during exposure to 1400 $\mu g/m^3$. No changes were observed. Predictable increases in heart rate, rectal temperature, ventilation and oxygen uptake were found but were not related to sulfate exposure, being simply the influence of the altered ambient conditions. Exposure to sulfuric acid mist in the 1 μm particle size range and in concentrations up to 1200 $\mu g/m^3$ had relatively minor effects on the cardiopulmonary system.

This report was submitted in fulfillment of grant R804853 by the Institute of Environmental Stress, University of California, Santa Barbara, under the sponsorship of the US Environmental Protection Agency. This report covers a period from April 1, 1977 to August 31, 1980, and work was completed as of August 31, 1980

CONTENTS

Foreword iii

Abstract iv

Figures vii

Tables viii

Abbreviations and Symbols ix

Acknowledgments x

1. Introduction 1
2. Conclusions 2
3. Recommendations 3
4. Review of Literature 4
5. Methods and Procedures 8
   - Subjects 8
   - Experimental Design 11
   - Protocol 11
   - Measurement Techniques 15
   - Exposure Facilities 16
   - Sulfate Analysis 20
   - Particle Size Classification 20
   - Sulfuric Acid Particle Generation 21
   - Control Conditions 23
6. Results 25
   - Actual Exposure Conditions 25
   - Pulmonary Function 25
   - Metabolic Measurements 31
7. Discussion 40

References 42

Glossary 44

Appendix - Sulfate Analysis; Turbidometric Barium Sulfate Method 61

FIGURES

Number		Page
1	Environmental chamber	17
2	Air conditioning system	19
3	Aerosol generator	22

TABLES

Number		Page
1	Description of Phase I Subjects	9
2	Description of Phase II Subjects	10
3	Experimental Design for H_2SO_4 Studies	12
4	Basic Protocol Followed in These Studies	13
5	Filtered Air Conditions	23
6	Exposure Chamber Conditions (Phase I)	26
7	Exposure Chamber Conditions (Phase II)	27
8	Pulmonary Function Before and After Exposure to Filtered Air and Sulfuric Acid Mist (Phase I, 0.9 μm Particles, 22°C, 55% RH)	28
9	Pulmonary Function Changes During Exposure to Filtered Air and Sulfuric Acid Mist (Phase I, 0.9 μm Particles, 22°C, 55% RH)	29
10	Pulmonary Function Measurements Before and After Exposure to Filtered Air and Sulfuric Acid Mist (Phase II, 0.9 μm Particles, 35°C, 85% RH)	32
11	Pulmonary Function Changes During Exposure to Filtered Air and Sulfuric Acid Mist (Phase II, 0.9 μm Particles, 35°C, 85% RH)	33
12	Metabolic Measurements During Exposure to Filtered Air and Sulfuric Acid Mist (Phase I, 0.9 μm Particles, 22°C, 55% RH)	35
13	Metabolic Measurements During Exposure to Filtered Air and Sulfuric Acid Mist (Phase II, 0.9 μm Particles, 35°C, 85% RH)	38

ABBREVIATIONS AND SYMBOLS

Because they are somewhat voluminous, the abbreviations and symbols used in this report have been placed at the rear (beginning on page 54), following the GLOSSARY to facilitate access and to avoid discontinuity of readership flow here.

ACKNOWLEDGEMENTS

The principal investigators acknowledge the important contributions of our most cooperative and willing subjects who obliging returned for repeated studies. We also acknowledge the assistance of the following, who aided immeasurably in the success of these long and complicated experiments:

J. F. Bedi
N. W. Boldum
B. L. Drinkwater
L. J. Folinsbee
J. A. Gliner
S. M. Horvath
J. A. Keyburn
J. A. Wagner

D. L. Batterton
D. M. Brown
J. B. Burnett
M. F. Bush
N. L. Cohen
C. L. Craig
N. S. Craig
D. A. D'Alfonso
J. C. Delehunt
L. S. Greos
N. J. Hamme
N. E. Iampietro
A. B. Loucks
D. L. Marsh
E. A. Shaw
P. A. Sorich
S. S. Wagner

INTRODUCTION

The presence of sulfuric acid in the atmosphere may actually increase with the necessity to utilize high sulfur fuels. The effects of sulfuric acid on vegetation and materials has been studied extensively. The effects of exposure to this pollutant on humans has only recently been subject to study and evaluation. Controlled exposures of subjects to various concentrations and particle size of this sulfate are needed to provide a base for evaluation of epidemiological studies -- and to determine potential health effects consequent to exposure. Clinical studies provide information consequent to acute exposures. Additional studies on repeated sequential exposures remain to be performed. It will also be necessary to evaluate potential synergistic effects of sulfuric acid in the presence of other air pollutants. The data reported herein represents an initial step and further investigations under controlled conditions are needed and required.

SECTION 2

CONCLUSIONS

No significant alterations in pulmonary functions or cardio-respiratory parameters were found in young male subjects exposed to sulfuric acid mist (exp to 1400 $\mu g/m^3$, particle size MMD 0.9 μm).

SECTION 3

RECOMMENDATIONS

1.) Studies utilizing sulfuric acid particles of $\cong$ 0.1 µm MMD need to be evaluated. Such studies are nearly completed and will be the subject of an upcoming report.

2.) Although no significant physiological effects were observed in the subjects studied in this report, there remain questions as to potential synergistic effects in the presence of other pollutants. Controlled experiments utilizing multiple pollutants (ozone, nitrogen dioxide, etc.) are needed. Community exposure is not to single pollutants but to multiple pollutants, each in variable concentrations.

3.) Similar exposure studies should be conducted on females, older individuals and patients suffering from pulmonary disorders.

SECTION 4

REVIEW OF LITERATURE

Amdur et al. (1952) found respiratory changes in all subjects exposed for 15 minutes to H_2SO_4 aerosol at concentrations of 0.35 mg/m^3 to 5 mg/m^3. Vapors from an electrically heated flask containing concentrated sulfuric acid were carried by compressed air into the main air stream and then into a plexiglass mixing chamber, delivering a mist of MMD 1 μm. The subjects breathed through a pneumotachograph, permitting measurement of inspiratory and expiratory flow rates. In 15 subjects, exposed to 0.35, 0.4, or 0.5 mg/m^3, the respiratory rate increased about 35% above control values, while the maximum inspiratory and expiratory flow rates decreased about 20%. Tidal volume decreased about 28% in subjects exposed to 0.4 mg/m^3. These changes occurred within the first 3 minutes of exposure and were maintained throughout the 15-minute exposure period. Lung function returned rapidly to baseline levels after the exposure ended. The tidal volume rose above control values during the first minute after termination of the exposure and then returned to pre-exposure levels. Breathing through the same apparatus without the acid mist was done as a control, and no such changes were observed. Some subjects showed a marked reaction to 5 mg/m^3. Individual responses were much more varied at this level, the main effect being a decrease in minute volume. These experiments do not indicate whether bronchoconstriction was the response to sulfuric acid, although the investigators suggest that this may be the case.

The effect of breathing sulfuric acid mist at different relative humidities (RH) was studied by Sim and Pattle (1957). Healthy males (variable number of subjects), 18 to 46 years of age, breathed 3 to 39 mg/m^3 concentrations of H_2SO_4 at 62% RH either via mask or exposure chamber. Subjects were also exposed in the chamber to 11.5 to 38 mg/m^3 concentrations at 91% RH.

At the lower RH, particles were 1 μm in size. The addition of water vapor to raise RH increased the mean particle size to 1.5 μm and intensified irritant effects of exposure. For example, the irritancy of wet mist of 20.8 mg/m^3 was much more severe ("almost intolerable at the onset") than that of the dry mist at 39.4 mg/m^3 ("well tolerated by all"). Air flow resistance ranged from 43 to 150% above normal in response to the wet mist, compared to increases ranging from 35.5 to 100% above normal in response to the dry mist. Two subjects exposed to sulfuric acid mist developed long-lasting bronchitic symptoms but may have been previously exposed to other substances. Adding ammonia to the acid mist annulled its irritant properties. There was no consistent evidence that the acid mist caused changes in respiratory functions or blood pressure, pulse rate, or other cardiovascular functions.

Toyama and Nakamura (1964) investigated the synergistic effects of SO_2 in combination with hydrogen peroxide (H_2O_2) aerosol mixtures, the latter of which oxidizes SO_2 to form H_2SO_4. SO_2 concentrations ranged from 1 to 60 ppm; the H_2O_2 concentrations were 0.29 mg/m^3 for particles of 4.6 μm CMD and 0.33 mg/m^3 for particles of 1.8 μm CMD. Airway resistance increased significantly in the combination (H_2SO_4) exposure, particularly for the group of 15 subjects inhaling the larger particles ($P < 0.01$). Toyama and Nakamura (1974) exposed subjects to a mixture of SO_2 and H_2SO_4 aerosols. They used an inadequate method to measure airway resistance. The diameter of the aerosols was 4-5 μm. They found a strong constricting effect on the upper airways.

Sackner et al. (1978) studied normal resting young adults and asthmatic middle-aged subjects who breathed, by mouth, either sodium chloride or sulfuric acid aerosols for 10 minutes at concentrations of 10, 100, and 1000 $\mu g/m^3$. Measurements on these individuals continued for up to 3 hours after exposure. The asthmatic patients represented a wide range of clinical status and

treatment. Neither normal nor asthmatic individuals showed significant alterations of lung volumes, distribution of ventilation, earoximetry, dynamic mechanics of breathing, oscillation mechanics of the chest-lung system, pulmonary capillary blood flow, diffusing capacity, arterial oxygen saturation, oxygen uptake, or pulmonary tissue volume. No delayed effects were observed during a follow-up period of a few weeks. The study indicated that single 10-minute exposures to a submicronic H_2SO_4 aerosol does not adversely affect normal or asthmatic adults.

Kleinman and Hackney (1978) and Avol et al. (1979) reported on the pulmonary responses of six normal and six asthmatic subjects exposed in an ambient environment of 88°F DB and 40% RH, and 94 $\mu g/m^3$ H_2SO_4. The asthmatics had pulmonary function test results which ranged widely from normal to abnormal. A sham exposure was followed by 2 consecutive days of acid exposure. Sufficient excess acid aerosol to neutralize the NH_3 present (about 56 μ/m^3 ammonia neutralization product) was added to the air to provide for the desired acid concentration (75 $\mu g/m^3$). The aerosol MMAD was approximately 0.48-0.81 μ. The effective exposure time was 2 hours, with the first 15 minutes of each half hour devoted to exercise which increased ventilation to twice the resting level. Only one subject was exposed at a time to minimize the effects of ammonia neutralization. The normal subjects showed no exposure-related changes. The lung functions of the asthmatics showed no significant changes. Two asthmatics, the extent of their disease not given, exhibited increases in respiratory resistance on both exposure days. Nonetheless, it was concluded that there were no convincing adverse short-term health effects of sulfuric acid. However, they also noted the small size of their subject pool and recommended additional studies.

Lippman et al. (1979) had 10 non-smokers inhale via nasal mask 0.5 μm (σ_g = 1.9) H_2SO_4 at 0, 100, 300, and 1,000 μg/m^3 for 1 hour. The exposures were random over the 4 days of testing. Pulmonary functions (assessed by body plethysmograph, partial forced expiratory maneuver, and nitrogen washout) were measured before, and 0.5, 2, and 4 hours post exposure. ^{99m}Tc-tagged Fe_2O_3 aerosol (7.5 μm MMAD) was inhaled 10 minutes before exposure for the determinations of lung retention of these particles. Tracheal mucus transport (TMTR) rates and bronchial mucociliary clearance were determined. No significant changes in respiratory mechanics or TMTR were observed following H_2SO_4 exposure at any level. However, bronchial mucociliary clearance halftime ($TM_{\frac{1}{2}}$) was altered depending on the concentration of H_2SO_4 inhaled. Bronchial clearance was increased ($P < 0.02$) following exposure to 100 μg/m^3 H_2SO_4. Following exposure to 1,000 μg/m^3, bronchial clearance was significantly ($P < 0.03$) reduced. Mucociliary transport in the airways distal to the trachea was affected more by H_2SO_4 exposure than was transport in the trachea. These investigators suggest that chronic H_2SO_4 exposures (at the concentrations they employed) could produce persistent changes in mucociliary clearance in previously healthy individuals and exacerbate pre-existing respiratory disease.

SECTION 5

METHODS AND PROCEDURES

SUBJECTS

Thirty male subjects were interviewed for this study. The procedures, protocol, and attendant risks of the study were explained to them and each gave his informed consent.* Eleven subjects participated in the first phase of the study (see PROTOCOL). Their physical characteristics are shown in Table 1. Nine subjects were lifetime non-smokers; two had smoked previously but had not smoked for at least one year prior to the study. Six subjects reported some type of allergy and three had a history of reacting to air pollution episodes. Seven of the subjects had previously resided in areas known to have significant quantities of air pollution (Los Angeles, New York). One subject had had "asthma" as a child. Nine subjects participated in Part II of the study (Table 2). All but one were lifetime non-smokers. Two subjects indicated a history of some type of allergy and one had had asthma as a child. Five of the nine previously resided in a polluted area and six reported some symptoms on previous exposure to ambient air pollutants. The remainder of the subjects participated in the studies to some degree but did not complete the requisite number of exposures. Therefore, their data are not included in this analysis.

---

* The nature and purpose of the study and the risks involved were explained verbally and given on a written form to each subjects prior to his voluntary consent to participate. The protocol and procedures for this study have been approved by the Committee on Activities Involving Human Subjects, of the University of California, Santa Barbara.

TABLE 1. DESCRIPTION OF PHASE I SUBJECTS

Subject No.	Ht (cm)	Wt (kg)	BSA (m^2)	Age (yr)	FVC (ml)	$FEV_{1.0}/FVC$ (%)	$\frac{FVC}{\text{Predicted FVC}}$ * (%)
1	178	70.3	1.87	22	5830	82.4	107.5
2	179	72.6	1.91	18	5536	86.8	94.6
3	185	79.4	2.03	19	6819	83.2	116.0
4	178	68.0	1.85	22	5502	95.6	99.7
5	187	77.0	2.02	24	5556	72.9	94.0
6	179	66.7	1.84	20	5102	84.4	91.8
7	163	66.8	1.72	20	5103	82.3	109.6
8	176	66.2	1.81	18	5153	88.7	94.7
9	185	70.3	1.92	19	4814	86.6	81.4
10	183	77.1	1.99	23	6379	72.7	111.4
11	185	68.0	1.90	25	5553	90.2	95.5
$\bar{X}$	180	71	1.90	21	5576	84.2	99.7
SD	6.69	4.74	0.09	2.43	589	6.84	10.3

* Anderson et al., 1968.

TABLE 2. DESCRIPTION OF PHASE II SUBJECTS

Subject No.	Ht (cm)	Wt (kg)	BSA (m^2)	Age (yr)	FVC (ml)	$FEV_{1.0}/FVC$ (%)	$\frac{FVC}{\text{Predicted FVC}}$ * (%)
1	172	72.4	1.85	19	4485	85.5	86.4
2	178	68.0	1.85	22	5502	95.6	99.7
3	183	77.3	2.00	20	5348	87.9	92.4
4	169	62.4	1.71	28	5128	75.1	106.0
5	173	66.7	1.80	20	4510	81.7	86.3
6	189	68.4	1.94	18	5807	80.1	93.8
7	175	60.1	1.73	18	4207	89.3	78.2
8	173	62.0	1.74	18	4561	94.8	86.5
9	171	70.1	1.82	18	5522	74.8	107.6
$\bar{X}$	176	67.5	1.83	20.1	5008	85.0	93.0
SD	6.4	5.5	0.10	3.3	574	7.7	9.9

* Anderson et al., 1968.

Each volunteer was medically screened. A battery of spirometric tests (forced vital capacity, functional residual capacity, maximum voluntary ventilation, and associated variables), a resting 12-lead electrocardiogram, a medical history questionnaire, and physical examination were used in evaluating each subject. In addition, each subject was familiarized with all test procedures in a separate session prior to beginning the experiments.

EXPERIMENTAL DESIGN

This study was designed to examine the effects of sulfuric acid particle concentration (mass/volume), particle size, and temperature and humidity on the pulmonary function of young male non-smokers. The first half of the study (Phases I and II) deals with larger particles in the range of 1 μm. The experimental design for this portion of the study is outlined in Table 3. There was an interval of at least one week between subject exposures.

In Phase I, each subject was exposed in random order to filtered air or 200, 400, or 800 $\mu g/m^3$ of particulate sulfuric acid. The actual levels of H_2SO_4 were somewhat higher. In Phase II, the same quantity of sulfate was used but the chamber temperature and humidity were raised to 35°C and 85% RH, respectively.

PROTOCOL (Table 4)

Repeated tests were made at the same time of day (i.e., either morning or afternoon) unless this could not be arranged for a given subject.

Upon arrival at the laboratory the subject was connected to the appropriate monitoring devices (e.g., ECG electrodes and/or rectal temperature probe). Pulmonary function tests, including forced vital capacity maneuvers (FVC, $FEV_{1.0}$, $FEV_{3.0}$, FEF50%, FEF75%,

TABLE 3. EXPERIMENTAL DESIGN FOR H_2SO_4 STUDIES

Large Particles (MMD ≅ 1 μm)		Small Particles (MMD ≅ 0.1 μm)	
Phase I	Phase II	Phase III*	Phase IV*
20°C, 45% RH	35°C, 85% RH	20°C, 45% RH	35°C, 85% RH
WVP† = 7.9 Torr	WVP† = 35.9 Torr	WVP† = 7.9 Torr	WVP† = 35.9 Torr

[DETAIL OF PHASE I SHOWN BELOW]

DETAIL OF PHASE I

Filtered Air	200 $\mu g/m^3$	400 $\mu g/m^3$	800 $\mu g/m^3$
< 10 $\mu g/m^3$	H_2SO_4	H_2SO_4	H_2SO_4

---

* Phase III and IV exposures are in process; will be completed shortly.

† Water Vapor Pressure.

TABLE 4. BASIC PROTOCOL FOLLOWED IN THESE STUDIES

PRE-EXPOSURE

1. Physical examination
2. Attach electrodes, thermocouple (if necessary)
3. Pulmonary function

Collins spirometer	3 x FVC	
	1 x FRC	
	1 x MVV	
Body plethysmograph	R_{aw}	
	TGV	
Wedge spirometer	3 x FVC	air
	3 x FVC	heliox

EXPOSURE

-1 min	Enter chamber Hook up leads Resting ECG
0 min	Begin walk
5 min	ECG (HR) & rectal temperature (T_{re})
10 min	ECG (HR) & T_{re}
15 min	ECG (HR), ventilation ($\dot{V}_E$), oxygen uptake ($\dot{V}_{O_2}$)
20 min	ECG (HR) & T_{re}
25 min	ECG (HR) & T_{re}
26 min	Pulmonary function (3 x FVC air; 3 x FVC heliox)
39 min	ECG (HR) & T_{re}
40 min - 80 min	Repeat sequence from 0-40 min
80 min - 120 min	Repeat sequence from 0-40 min

POST-EXPOSURE

1. Pulmonary function tests
   Repeat pre-exposure tests
2. Physical examination
3. Remove monitoring devices
4. Symptom questionnaire (verbal)

FEF25-75%, FEF75-85%), lung volumes (IC, ERV, FRC), maximum voluntary ventilation (MVV), body plethysmography (R_{aw}, TGV), and helium-oxygen FVC, were performed prior to the experiment. Some of the tests were performed inside the chamber before any sulfate had been added to the chamber air.

Following the establishment of the appropriate sulfate concentration within the exposure chamber, the subject entered and began to walk on a treadmill (Quinton) at 3.5 miles/h at a slope which was sufficient to elicit a ventilation of approximately 30 ℓ/min BTPS. The exercise period lasted 20 min. During the last 5 min of exercise, the subject breathed through a mouthpiece to enable collection of expired air for determination of ventilation volume and oxygen uptake.

Following the exercise periods, the subject rested 5 min and then performed forced vital capacity tests breathing first air and then a helium-oxygen mixture. For each gas mixture, three forced vital capacity maneuvers were recorded and associated variables ($FEV_{1.0}$, FEF25-75%, FEF75-85%, FEF50%, FEF75%) were calculated. Prior to the start of the next exercise period, a resting heart rate was obtained.

The above sequence, performed in the first 40 min of exposure, was repeated twice more in the next 80 min of the exposure period.

At the end of the exposure, the subject exited the chamber. The sequence of pre-exposure pulmonary function tests was repeated. The monitoring leads were detached and the subject was examined by the attending physician. Finally, the subject was interviewed regarding any symptoms he may have experienced during the exposure.

MEASUREMENT TECHNIQUES

Pulmonary function tests were performed in the standing position. A 13.5-liter Benedict-Roth type spirometer was used for the determination of lung volumes (VC, IC, ERV), forced expiratory parameters (FVC, $FEV_{1.0}$, $FEV_{2.0}$, $FEV_{3.0}$, FEF50%, FEF75%, and FEF25-75%), and MVV. Functional residual capacity was determined by a helium dilution technique. A wedge spirometer was also used for determination of forced expiratory measures for tests performed within the chamber. A large polyethylene bag was connected to a breathing valve to supply heliox during the heliox FVC test. The difference between flow at 75% of VC expired in the air and heliox tests (ΔFEF75%) and the point at which the maximum expired flow first became equal (PIF) was calculated from the flow-volume tracings of the respective best effort using air or heliox. Thoracic gas volume (TGV) and airway resistance (R_{aw}) were measured in a constant-volume body plethysmograph using the method of DuBois et al. (1956a, 1956b). All flows and volumes were corrected to BTPS. Both spirometers were interfaced with a PDP-11/60 laboratory computer which provided on-line analysis of the pulmonary function tests. Ventilation volume was determined by having the subject breathe through a low-resistance breathing valve into a chain-compensated 120-liter spirometer. Respiratory frequency was determined from a continuous recording of expired carbon dioxide concentration or a thermocouple in the expired line. Cardiac frequency was determined from the electrocardiogram (reciprocal of the mean R-R interval for six beats). Standard open-circuit methods were used for determination of oxygen consumption. Expired gas aliquots sampled directly from a mixing chamber were analyzed for oxygen and carbon dioxide by gas chromatograph (Quintron).

EXPOSURE FACILITIES

The initial phase of the project was devoted to modifying the exposure chamber and air-conditioning system to improve air turnover and climatic control and to eliminate potential sources of aerosol contamination. The present facility for human subject exposure to atmospheric contaminants will be described in the following four sections: 1) Exposure Chamber, 2) Ambient Air Contamination Removal, 3) Air Conditioning, and 4) Filtration.

Exposure Chamber

The environmental exposure chamber (Fig. 1) is constructed of two walls of acrylic resin plastic separated by 1 inch of polystyrene insulation. The internal dimensions of the chamber are 1.8 x 2.4 x 2.6 meters. A vinyl tile floor is raised 4 inches above the concrete building floor. Two walls and the door are insulated to one-half of their height in order to provide visual inspection of subjects and conditions. The chamber air inlet is an insulated mixing box located above the top right-hand front corner of the chamber. Air is removed through a vent located in the bottom left rear corner of the room 2 inches above the floor. Further mixing of the inlet air stream is provided by two small fans directed across the inlet. The chamber is illuminated by fluorescent fixtures and communication is maintained by an intercom system. Sealed ports in the chamber wall provide for sample lines to cardiovascular and pulmonary measures, pollution monitors, and filter collection trains.

Chamber temperatures can be maintained between 19 and 55°C ± 1°C and relative humidity between 30 and 99% ± 2.5% at 100 cfm air inflow. The chamber is maintained at less than 0.01 inch of water pressure positive with respect to ambient.

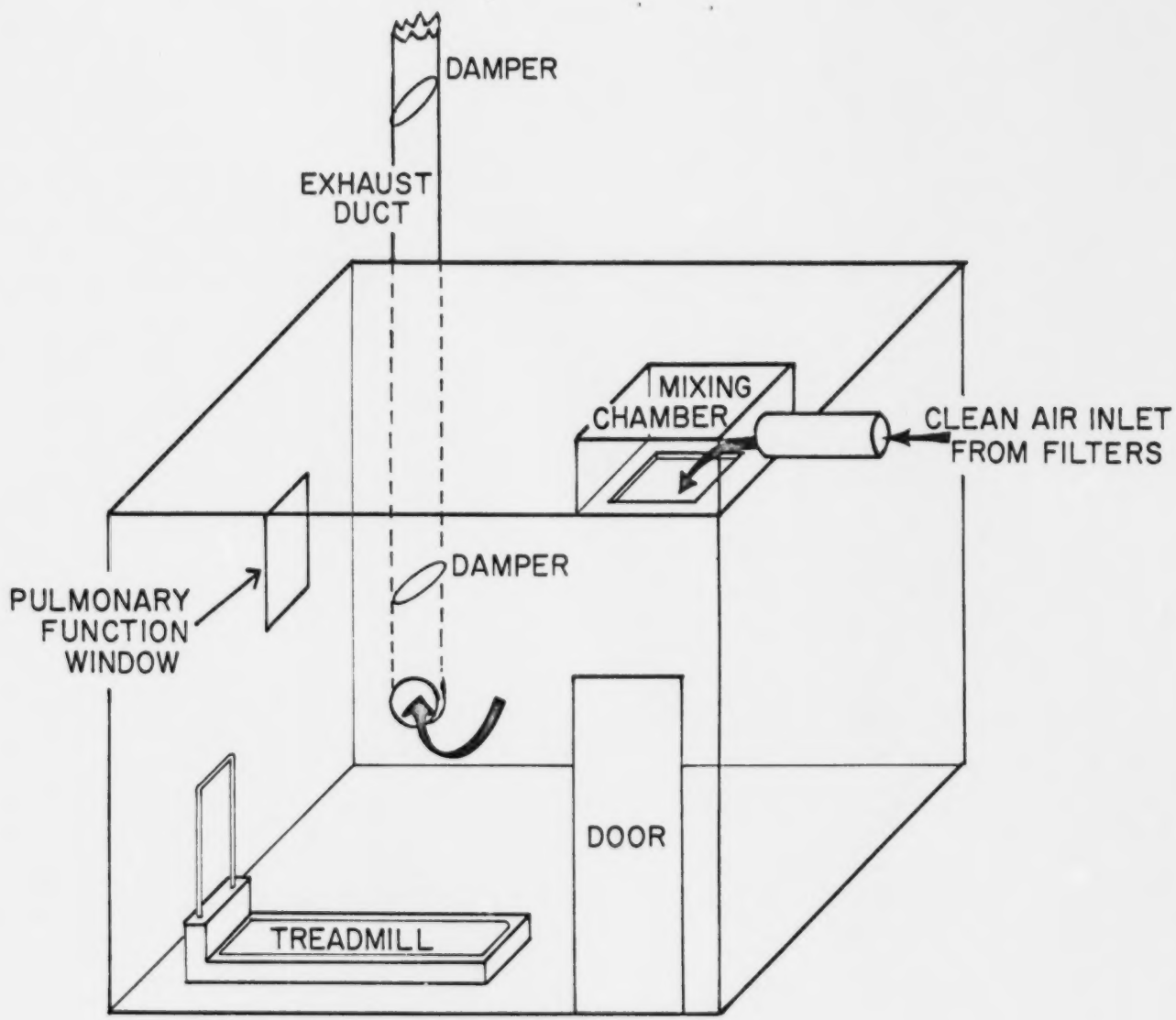


Figure 1. ENVIRONMENTAL CHAMBER

Air Conditioning

Air conditioning is provided by a custom-designed air-conditioner unit (BEMCO DTHS + 15/45C-2) (Fig. 2). The air stream is cooled to remove excess moisture and is limited by a 32°F dew point. Stainless-steel sheathed heaters are used to obtain the required chamber temperature conditions. Steam produced by heating filtered de-ionized water in a stainless-steel container is intermittently injected into the air plenum to produce the appropriate moisture content. The air conditioner can provide up to 600 cfm of air for ambient conditions of 65°F to 120°F with relative humidities from the dew point limit to 100%. However, with the filtration and contaminant apparatus attached, the maximum air delivery is approximately 150 cfm.

Filtration

To remove dust and particulate matter, a series of filtration boxes were used (Fig. 2). The first filtration container was placed immediately after the ambient contamination removal unit and contains three filters: (a) 4-inch Farr 30/30 deep-pleated rigid filters 30 to 35% efficient (ASHRAE 52-68) with an arrestance rate of 92%, (b) a 12-inch Farr HB-15 rigid extended area filter with an efficiency rating of 50 to 55% and an arrestance rate of 97% (ASHRAE 52-68), and (c) a 12-inch HEPA filter — a rigid extended area type with an efficiency rating of 99.95%.

The second filtration box is placed in the air stream just upstream of the chamber. A 12-inch Farr HB-15 and a 12-inch Farr HP-100, which is a rigid extended area filter, with efficiency and arrestance rating of 80-85% and 98% (ASHRAE), respectively, are contained in this unit. The air stream then enters an insulated mixing box on the top of the environmental chamber, where the air pollutants are added to the chamber air inlet stream. All ducting is via 6-inch PVC pipe except for the air-conditioning unit, where stainless steel is used.

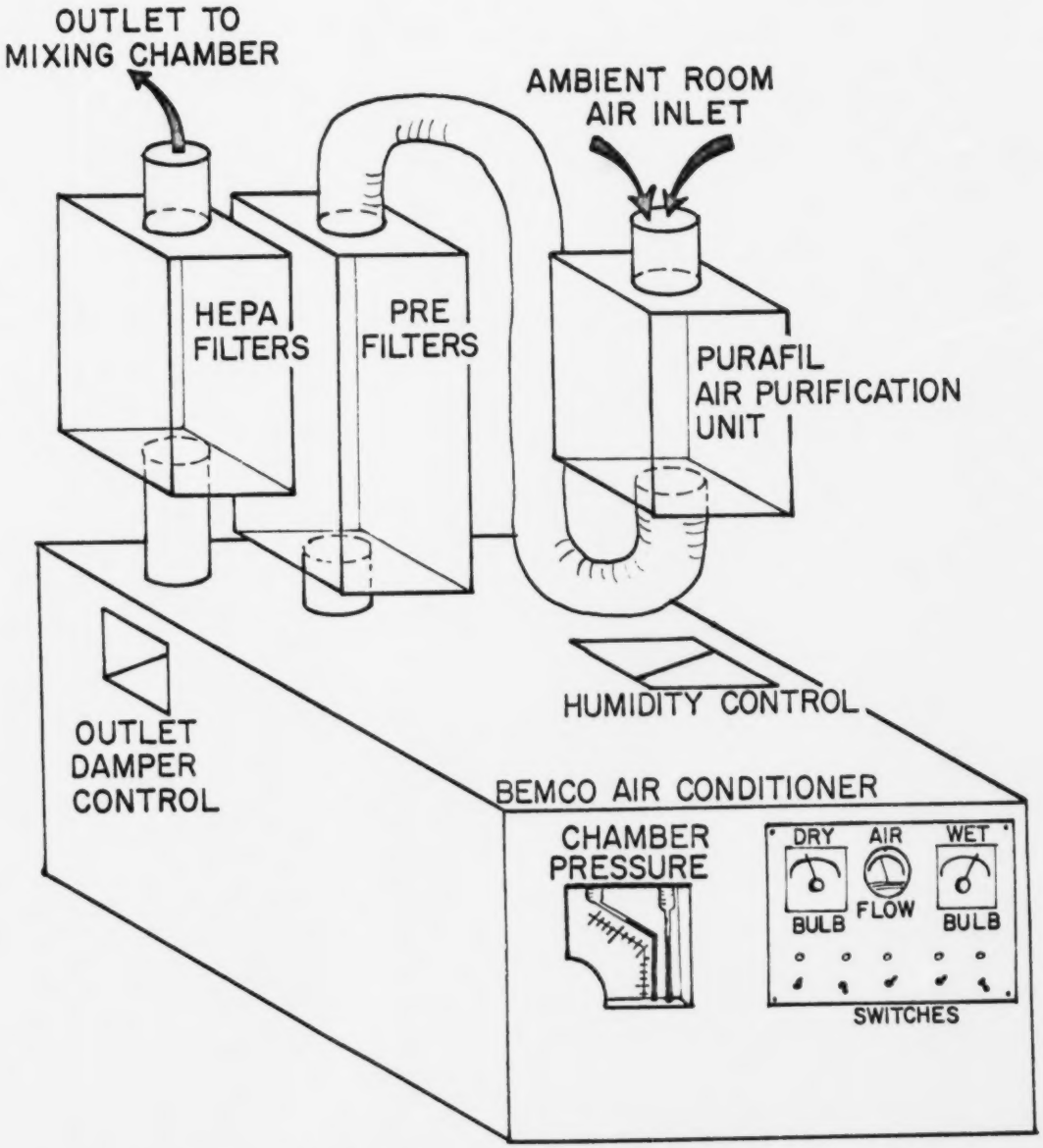


Figure 2. AIR CONDITIONING SYSTEM

SULFATE ANALYSES

Chemical Analysis for Sulfate

Two separate wet chemical methods for the analysis of sulfate were tested in the laboratory — the sodium rhodizonate method (Swaroop, 1973) and the turbidimetric/nephelometric barium sulfate method (Air and Industrial Hygiene Laboratory, 1965). We selected the AIHL method for use in this project. A description of the technique and error analysis is contained in the Appendix.

Sulfate samples were collected on Gelman type AE glass fiber filters (99.9% efficiency to 0.3 μm particles) which were pretreated to remove interfering trace sulfate (see Appendix).

Filters were collected from one of the dual ports located near the chamber exhaust. A 47-mm open-face and 47-mm in-line aluminum filter holders (Gelman) were placed in series and inserted into the chamber. Sample flow was regulated (with a Sierra Instruments sample pump) to maintain a constant vacuum pressure and thus maintain a constant flow independent of filter loading. The sample flow was calibrated against a 13.5-liter spirometer and the sample train was leak-tested.

Instrumental Analysis for Sulfate

A Monitor Labs sulfur monitor was also used to determine atmospheric sulfate levels. This instrument does not respond quantitatively to sulfate concentration but provides a qualitative estimate.

PARTICLE SIZE CLASSIFICATION

The size classification was performed by impaction procedures. An IBC (Berkeley Instruments) 10-stage cascade impactor utilizing quartz crystal microbalances as the impaction plates in each stage was used since it provides a reasonable range of detection for the desired particle range. The 50% cutoff diameters range from

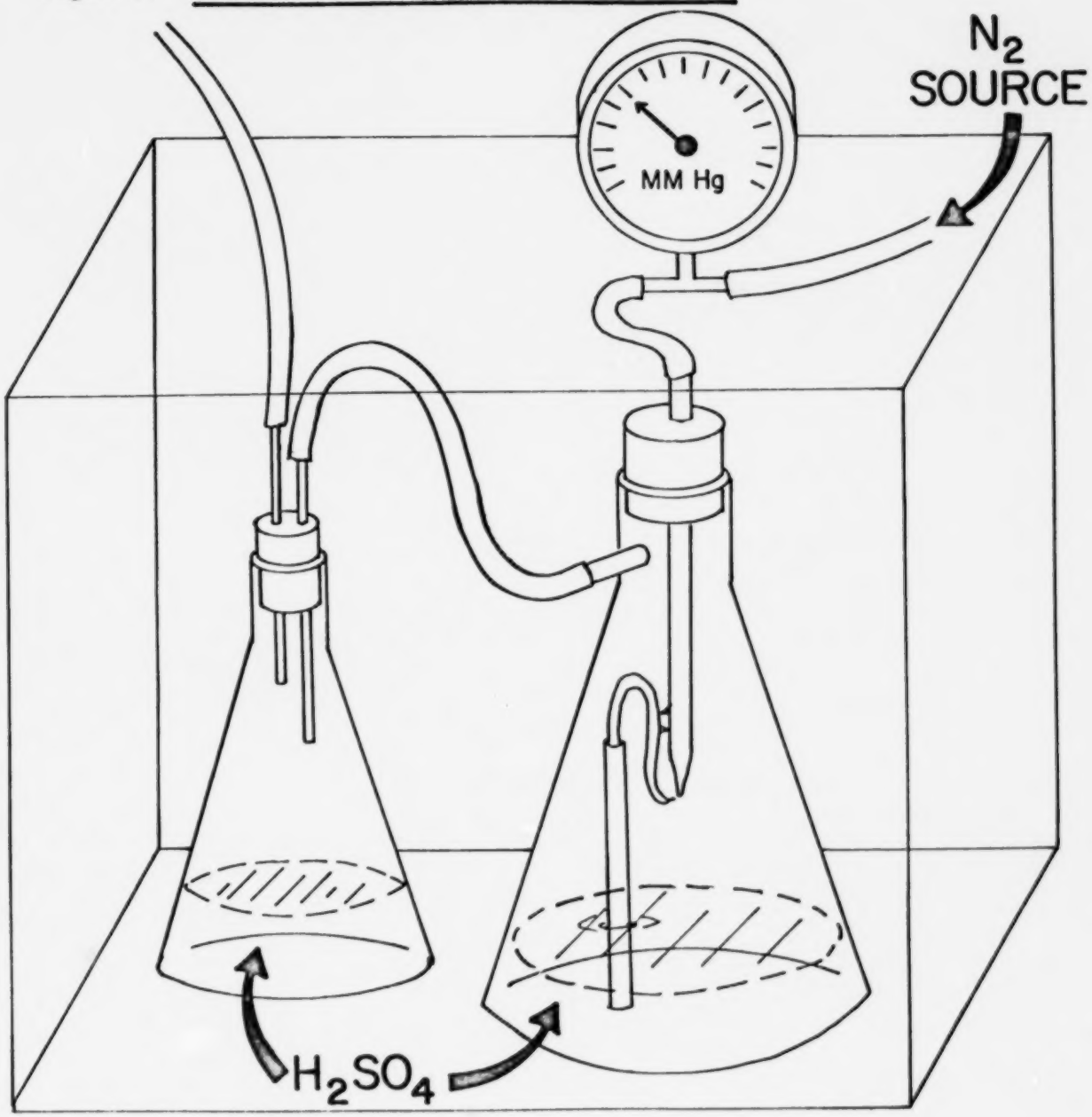
0.05 μm for the last stage to 25 μm for the first stage. The temperature variation of the oscillating frequency of a single crystal is controlled by measuring the beat frequency between the impaction crystal and a mating crystal located in the same stage. Thus the weight of the impacted aerosol is proportional to a change in this beat frequency. Particle bounce was minimized by coating each crystal surface by apiezon grease.

Since the mass of aerosol deposited is proportional to a change in beat frequency, the stability of this frequency in a no-flow situation is critical; therefore, several test runs were made to assess the crystal frequency stability. A stability check was performed before each test for a short time period in a zero flow state. The stability criterion was less than four counts change in a 20-min test.

SULFURIC ACID PARTICLE GENERATION

Sulfuric acid aerosol with a mass median diameter of approximately 1 μm was generated using a modification of the procedure described by Walters (1976). The micron-sized particles are produced by nebulization of sulfuric acid whose concentration was in equilibrium with the water vapor pressure of the exposure chamber. Thus the aerosol droplet should neither grow nor shrink in size by acquiring or losing water to the environment, and droplet composition thus remains constant. The nebulizer draws H_2SO_4 from a bath by Bernoulli's principle into the air stream, where nebulization occurs. A second flask was used as a trap where large particles are removed by impaction (Fig. 3). Filtered extra dry grade nitrogen was used for nebulization and as the carrier gas. At a nebulizer driving pressure of 2.5 psi the sulfate exceeded 1000 $\mu g/m^3$; thus the approximate operating pressure range was from 1.25 to 2.5 psi, and a large number of calibration runs were performed in this range. The sulfate level was raised to one of the target concentrations (200, 400, 800 $\mu g/m^3$) for 45 min and then a filter sample was taken. These measurements

Figure 3. AEROSOL GENERATOR



were then correlated with simultaneous readings taken from the sulfur monitor. The sulfur monitor values were used as a guide in controlling chamber sulfate levels since they provide qualitative information regarding sulfate concentration, but we do not regard these values as quantitatively accurate due to loss of sample in the instrument's burner block. The sulfate monitor was calibrated with a certified sulfur dioxide permeation tube (Monitor Labs).

CONTROL CONDITIONS

Prior to the initiation of these studies we performed clean air studies on the chamber on 10 separate days. The chamber atmosphere was monitored for ozone (MacMillan chemiluminescent monitor and Dasibi UV photometer), sulfur dioxide (Monitor Labs sulfur monitor), nitrogen oxides (Monitor Labs NO/NO_x monitor), and total particulates and particle size (IBC Celesco electronic cascade impactor). The results are shown in Table 5.

TABLE 5. FILTERED AIR CONDITIONS

O_3	$\leq$	0.004	$\pm$	0.003 ppm
SO_2	$\leq$	0.000	$\pm$	0.000 ppm
NO_x	$\leq$	0.005	$\pm$	0.004 ppm
Particulates	$\leq$	1.8	$\pm$	0.9 $\mu g/m^3$

DATA ANALYSIS

Data were analyzed by a series of analyses of variance. A two-factor analysis of variance was used for pre-exposure/post-exposure comparisons with repeated measures across time and ambient environment. Similarly, data were analyzed across time during the exposure. Separate analyses were made for Phase I and Phase II conditions, but comparisons were not made across temperature and humidity conditions. In all cases where a significant interaction

was observed, a test was made of the simple main effects followed by a Newman-Keuls test of ordered means where appropriate.

Linear regression analysis was performed comparing the percentage decrease (Pre/Post) of each pulmonary function variable with the actual sulfate concentration to which the subject was exposed.

SECTION 6

RESULTS

ACTUAL EXPOSURE CONDITIONS

Phase I

The average values for sulfate concentration (filter samples), particle size (mass median diameter and geometric standard deviation), temperature, and humidity are shown in Table 6.

Phase II

The average values for sulfate concentration, particle size, temperature, and humidity are shown in Table 7. The variability of chamber concentrations increased somewhat under the higher humidity conditions.

PULMONARY FUNCTION

Phase I

The results of pre- and post-exposure pulmonary function tests are shown in Table 8. Forced vital capacity (FVC), forced expired volume in 3 seconds ($FEV_{3.0}$), and inspiratory capacity (IC) decreased following exposure under all exposure conditions, including filtered air. There was thus no effect of sulfate on these changes. $FEV_{1.0}$ was decreased only following exposure to 939 $\mu g/m^3$ of sulfate. This observation was not substantiated by changes in other associated variables. Indeed, the forced expiratory flow at 50% of vital capacity (FEF50%) was increased following exposure to 223 and 418 $\mu g/m^3$ sulfate.

Pulmonary function measurements taken during the exposure period (Table 9) showed similar effects to those seen in the pre and post measurements. FVC, $FEV_{3.0}$, and IC were larger at the beginning than at the end of exposure. Again there was no interaction due to sulfate exposure.

TABLE 6. EXPOSURE CHAMBER CONDITIONS (PHASE I)

		Nominal SO_4 Level		
	Filtered Air	200 $\mu g/m^3$	400 $\mu g/m^3$	800 $\mu g/m^3$
SO_4 ($\mu g/m^3$)	< 5	223 (160-288)	418 (306-549)	939 (704-1216)
Particle size (μm)	---	0.93	0.91	0.91
Geometric SD	---	1.73	1.71	1.66
Temperature (°C)	22.8	22.5	21.9	22.0
Humidity (%)	51	57	54	53

TABLE 7. EXPOSURE CHAMBER CONDITIONS (PHASE II)

		Nominal SO_4 Level		
	Filtered Air	200 $\mu g/m^3$	400 $\mu g/m^3$	800 $\mu g/m^3$
SO_4 ($\mu g/m^3$)	< 5	314 (231-459)	600 (333-954)	1107 (689-1464)
Particle size (μm)	---	0.93	0.93	0.81
Geometric SD	---	1.66	1.72	1.78
Temperature (°C)	34.9	35.0	35.0	35.2
Humidity (%)	83.7	83.4	83.5	84.3

TABLE 8. PULMONARY FUNCTION BEFORE AND AFTER EXPOSURE TO FILTERED AIR AND SULFURIC ACID MIST (PHASE I, 0.9 μm PARTICLES, 22°C, 55% RH) (VALUES ARE MEANS ± STANDARD DEVIATION)

	Pre-Exposure				Post-Exposure			
		H_2SO_4 Concentration ($\mu g/m^3$)				H_2SO_4 Concentration ($\mu g/m^3$)		
	Filtered Air	223	418	939	Filtered Air	223	418	939
FVC (ml)	5638±584*	5646±550*	5657±613*	5653±620*	5579±564	5536±628	5586±634	5466±601
$FEV_{1.0}$ (ml)	4772±456†	4825±539	4716±553†	4817±570‡	4789±497	4797±566	4760±552	4716±572§
$FEV_{3.0}$ (ml)	5585±585*	5608±569*	5612±618*	5622±628*	5550±570	5514±640	5540±633	5442±572
FEF25-75% (ℓ/s)	4.97±0.69	5.14±0.89	4.97±0.74	5.11±0.88	5.06±0.81	5.36±1.11	5.05±0.80	5.29±1.08
FEF75-85% (ℓ/s)	2.12±0.59	2.20±0.54	2.29±0.61	2.13±0.68	2.22±1.02	2.32±0.72	2.32±0.70	2.28±0.71
FEF50% (ℓ/s)	5.57±0.77	5.85±1.01#	5.48±0.85#	5.82±0.97	5.63±1.03	6.12±0.98#	5.84±0.96#	5.81±1.15
FEF75% (ℓ/s)	2.80±0.65	2.83±0.57	2.83±0.68	2.76±0.61	2.93±0.80	3.05±0.90	2.88±0.77	2.89±0.73
IC (ml)	3622±476*	3582±489*	3605±545*	3535±496*	3478±454	3491±578	3488±455	3402±462
ERV (ml)	2016±449	2015±364	2052±470	2118±391	2101±447	2045±383	2117±449	2064±397
FRC (ml)	3655±739	3684±734	3725±695	3745±738	3726±723	3764±699	3795±764	3759±729
RV (ml)	1639±426	1669±474	1672±366	1626±432	1625±395	1719±462	1678±561	1696±487
MVV (ℓ/min)	202±34	206±35	199±35	211±35	205±34	202±41	204±39	209±32
R_{aw} (cm $H_2O \cdot \ell^{-1} \cdot s^{-1}$)	1.67±0.39	1.73±0.35	1.75±0.52	1.87±0.48	1.76±0.58	1.77±0.57	1.64±0.46	1.69±0.41
PIF (ℓ)	1.03±0.84	0.94±0.61	1.15±0.65	0.80±0.64	0.85±0.69	0.78±0.44	0.75±0.45	0.71±0.50

* Pre > Post across all conditions. No pollutant effect. † Pre code 1,3 < Pre code 2,4. ‡ Pre > Post.

§ Post 939 $\mu g/m^3$ < Post 223 $\mu g/m^3$. # Post > Pre.

TABLE 9. PULMONARY FUNCTION CHANGES DURING EXPOSURE TO FILTERED AIR AND SULFURIC ACID MIST (PHASE I, 0.9 μm PARTICLES, 22°C, 55% RH) (VALUES ARE MEANS ± STANDARD DEVIATION)

		H_2SO_4 Concentration ($\mu g/m^3$)			
		Filtered Air	223	418	939
FVC (ml)	Pre-exposure	5353±543*	5247±554*	5297±543*	5281±590*
	25 min post	5214±613	5250±562	5208±582	5196±595
	65 min post	5247±620	5208±556	5243±558	5174±611
	110 min post	5162±619	5228±570	5167±529	5134±619
$FEV_{1.0}$ (ml)	Pre-exposure	4647±486	4534±509	4513±571	4546±567
	25 min post	4481±542	4430±637	4426±588	4494±554
	65 min post	4531±577	4554±534	4515±485	4437±552
	110 min post	4518±519	4565±643	4532±534	4477±565
$FEV_{3.0}$ (ml)	Pre-exposure	5326±555*	5220±555*	5284±548*	5259±588*
	25 min post	5185±610	5192±603	5121±589	5163±592
	65 min post	5227±631	5175±588	5192±564	5150±623
	110 min post	5133±614	5199±574	5139±538	5102±620
IC (ml)	Pre-exposure	3475±483*	3387±508*	3434±433*	3425±535*
	25 min post	3253±592	3234±580	3337±489	3293±459
	65 min post	3293±434	3317±546	3305±487	3213±491
	110 min post	3186±420	3356±598	3256±450	3224±482

(CONTINUED ON NEXT PAGE)

* Main effect Pre > all other time periods.

TABLE 9 (continued)

		Filtered Air	H_2SO_4 Concentration ($\mu g/m^3$)		
			223	418	939
FEF25-75% (ℓ/s)	Pre-exposure	4.92±0.79	4.91±0.83	4.75±0.97	4.90±0.83
	25 min post	4.73±0.83	4.82±1.21	4.64±0.97	4.90±0.84
	65 min post	4.90±1.01	5.13±1.05	4.81±0.89	4.84±0.95
	110 min post	5.05±0.83	5.10±1.30	4.90±0.88	5.02±0.90
FEF50% (ℓ/s)	Pre-exposure	4.80±0.83	4.99±0.78	4.69±0.99	4.92±0.85
	25 min post	4.73±0.81	4.76±1.14	4.54±0.94	5.00±0.86
	65 min post	4.88±0.98	4.98±0.84	4.76±0.91	4.92±0.89
	110 min post	5.05±0.80	5.03±1.08	4.83±0.93	5.00±0.92
FEF75% (ℓ/s)	Pre-exposure	2.53±0.61	2.66±0.70	2.40±0.74	2.54±0.58
	25 min post	2.51±0.71	2.50±0.65	2.48±0.84	2.56±0.57
	65 min post	2.53±0.84	2.64±0.77	2.47±0.72	2.52±0.68
	110 min post	2.65±0.73	2.66±0.87	2.63±0.78	2.59±0.66

Phase II

Under hot-humid conditions, forced vital capacity decreased significantly post-exposure in all conditions (Table 10). However, maximum voluntary ventilation increased following exposure. Both FEF75% and FEF75-85% showed a tendency to increase following exposure. The only significant interaction for pollutant across time was seen for FEF75%, where the post-exposure value was greater than the pre-exposure value under filtered air conditions but not during sulfate exposure. This observation was not corroborated by changes in FEF75-85%, which increased post-exposure under all conditions.

Pulmonary function measured during exposure is shown in Table 11. There was a significant decrease in FVC across time but this was not related to pollutant exposure. Because of the considerable variation in sulfate concentrations within exposure groups, the data were subjected to regression analysis. Individual changes in pulmonary function tests from pre- to post-exposure were correlated with the concentration of sulfate to which the subject was exposed. None of the correlations approached significance. Examination of the data from the three subjects exposed to 1400 $\mu g/m^3$ revealed no changes.

METABOLIC MEASUREMENTS

Phase I

Exercising metabolic variables measured at three intervals during the exposure are summarized in Table 12. Ventilation, oxygen uptake, and ventilatory equivalent for carbon dioxide tended to increase slightly towards the end of exposure so that an overall difference ($P < 0.05$) was seen between measures made at 55 min and those at 95 min of exposure. The increase in ventilation was accompanied by a slight diminution of tidal volume and a decrease in the respiratory exchange ratio. The only significant difference which was related to

TABLE 10. PULMONARY FUNCTION MEASUREMENTS BEFORE AND AFTER EXPOSURE TO FILTERED AIR AND SULFURIC ACID MIST (PHASE II, 0.9 μm PARTICLES, 35°C, 85% RH)

	Filtered Air		H_2SO_4 Concentration ($\mu g/m^3$)					
			314		600		1107	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post
FVC (ml)	5114±752	5023±695*	5043±694	4947±653*	5085±735	4972±626*	5090±738	4932±678*
$FEV_{1.0}$ (ml)	4333±517	4425±472	4264±425	4176±411	4314±613	4305±417	4327±521	4261±628
$FEV_{3.0}$ (ml)	5074±736	4982±687	4994±658	4850±631	5020±655	4942±597	5030±730	4919±678
RV (ml)	1397±448	1542±477	1455±418	1481±437	1485±476	1499±372	1524±457	1550±477
FEF25-75% (ℓ/s)	4.72±1.22	5.27±1.12	5.01±1.50	4.88±1.58	4.93±1.11	4.76±0.92	4.76±1.02	4.83±1.22
MVV (ℓ/min)	186.3±32.8	201.6±30.1†	188.1±36.5	195.0±37.3†	185.1±37.1	197.6±41.1†	188.5±30.5	194.1±35.7†
FEF50% (ℓ/s)	5.05±1.12	5.58±1.00	5.42±1.22	5.40±1.32	4.91±1.05	5.30±1.09	5.31±1.28	5.38±1.35
FEF75% (ℓ/s)	2.45±0.65	3.21±1.05‡	2.56±0.67	2.64±0.95	2.73±0.72	2.67±0.61	2.56±0.66	2.79±0.87
FEF75-85% (ℓ/s)	1.93±0.40	2.47±0.82*	2.02±0.64	2.11±0.74*	2.13±0.60	2.24±0.65*	1.98±0.70	2.04±0.82*
R_{aw} (cm $H_2O \cdot \ell^{-1} \cdot s^{-1}$)	1.81±0.37	1.76±0.43	1.52±0.42	1.92±0.20	1.59±0.46	1.74±0.28	1.70±0.34	1.55±0.62
TGV (ml)	3852±918	3839±845	3976±795	3797±952	4122±1011	3849±941	3745±900	4064±924

*Pre > Post. †Post > Pre. ‡Filtered Air Post > Pre; Filtered Air Post > Post in 314, 600, 1107 $\mu g/m^3$.

TABLE 11. PULMONARY FUNCTION CHANGES DURING EXPOSURE TO FILTERED AIR AND SULFURIC ACID MIST (PHASE II, 0.9 μm PARTICLES, 35°C, 85% RH) (VALUES ARE MEANS ± STANDARD DEVIATION)

			H_2SO_4 Concentration ($\mu g/m^3$)		
		Filtered Air	314	600	1107
FVC (ml)	Pre-exposure	5077±568*	5065±657*	4981±687*	5123±704*
	25 min post	4998±628	4963±637	4906±714	4971±674
	65 min post	4922±733	4871±721	4875±561	4840±697
	110 min post	4928±633	4787±679	4878±638	4789±608
$FEV_{1.0}$ (ml)	Pre-exposure	4341±443	4417±469	4328±613	4444±529
	25 min post	4510±529	4314±582	4291±555	4385±575
	65 min post	4364±562	4238±511	4286±485	4306±623
	110 min post	4421±536	4200±619	4359±552	4241±630
FEF25-75% (ℓ/s)	Pre-exposure	5.01±1.22†	5.19±1.29	4.83±1.29	4.89±1.10
	25 min post	5.57±1.29†	4.85±0.96	5.05±1.16	5.29±1.02
	65 min post	5.56±1.28†	5.23±1.22	5.19±1.20	5.35±1.39
	110 min post	5.79±1.29†	5.21±1.38	5.32±1.29	5.46±1.55
FEF50% (ℓ/s)	Pre-exposure	5.81±1.62	5.87±1.59	5.36±1.56	5.64±1.46
	25 min post	6.36±1.49	5.58±1.01	5.75±1.42	5.96±1.45
	65 min post	6.20±1.26	5.92±1.25	5.79±1.56	5.86±1.81
	110 min post	6.41±1.38	5.83±1.77	5.91±1.31	6.32±1.73

(CONTINUED ON NEXT PAGE)

* FVC decreased significantly across time.

† Filtered air values greater than 314 or 600 $\mu g/m^3$.

TABLE 11 (continued)

		H_2SO_4 Concentration ($\mu g/m^3$)			
		Filtered Air	314	600	1107
FEF75% (ℓ/s)	Pre-exposure	2.85±0.93	3.05±1.13	2.90±1.04	2.73±0.73
	25 min post	3.51±1.08	2.54±0.89	2.83±1.10	2.98±0.91
	65 min post	3.19±1.19	2.90±1.09	3.12±0.87	3.05±1.25
	110 min post	3.35±1.21	2.94±1.25	3.00±0.96	3.12±1.39
ΔFEF75% (ℓ/s)	Pre-exposure	0.87±0.47	0.57±0.45	0.57±0.49	0.73±0.48
	25 min post	0.60±0.86	0.83±0.47	0.85±0.73	0.92±0.44
	65 min post	0.99±0.49	0.71±0.54	0.78±0.77	0.59±0.90
	110 min post	0.82±0.63	0.86±0.46	0.66±0.84	0.92±0.41
Point of identical flow (ml)	Pre-exposure	589.5±503.3	563.5±491.6	686.3±381.3	580.4±460.0
	25 min post	1148.8±786.6	729.6±312.9	758.1±444.7	349.9±385.6
	65 min post	552.9±620.3	790.4±684.2	866.8±784.5	564.0±543.9
	110 min post	736.9±767.0	464.6±349.7	612.9±486.3	666.4±340.7

TABLE 12. METABOLIC MEASUREMENTS DURING EXPOSURE TO FILTERED AIR AND SULFURIC ACID MIST (PHASE I, 0.9 μm PARTICLES, 22°C, 55% rh) (VALUES ARE MEANS ± STANDARD DEVIATION)

			H_2SO_4 Concentration ($\mu g/m^3$)		
	Time	Filtered Air	223	418	939
Ventilation (ℓ/min BTPS)	15 min	31.41±2.05	31.83±1.49	32.44±2.41	33.65±4.50
	55 min	31.39±2.21	31.76±1.99	31.78±3.21	32.85±3.45
	95 min	32.56±2.14*	32.49±2.17*	32.83±2.66*	32.89±4.71*
Tidal volume (ml BTPS)	15 min	1585±455†	1561±435†	1508±368†	1601±403†
	55 min	1575±370	1472±429	1499±396	1501±338
	95 min	1573±341	1453±358	1496±432	1477±371
Respiratory frequency (breaths/min)	15 min	21.0±4.7‡	21.6±5.0	22.5±5.0	21.9±4.4
	55 min	20.7±4.1‡	23.0±5.8	22.3±4.9	22.8±5.2
	95 min	21.5±4.6‡	23.4±4.8	23.2±5.1	23.3±5.4
Oxygen uptake (ℓ/min STPD)	15 min	1.36±0.09	1.40±0.14	1.41±0.12	1.43±0.20
	55 min	1.37±0.11	1.39±0.14	1.38±0.14	1.43±0.19
	95 min	1.40±0.09*	1.40±0.13*	1.44±0.12*	1.44±0.19*

(CONTINUED ON NEXT PAGE)

* 95 min > 55 min. † 15 min > 95 min. ‡ Filtered air < all H_2SO_4 exposures.

§ 95 min < 55 min < 15 min.

TABLE 12 (continued)

	Time	Filtered Air	H_2SO_4 Concentration ($\mu g/m^3$) 223	418	939
V.E. CO_2 ($\ell \cdot min^{-1} \cdot \ell CO_2^{-1}$)	15 min	25.9±1.7	26.3±1.2	26.8±2.0	27.7±3.7
	55 min	25.9±1.8	26.2±1.7	26.2±2.6	27.1±2.8
	95 min	26.9±1.7*	26.8±1.8*	27.1±2.2*	27.2±3.9*
Respiratory exchange ratio	15 min§	0.86±0.05	0.83±0.02	0.82±0.05	0.85±0.04
	55 min§	0.84±0.05	0.82±0.03	0.82±0.04	0.83±0.03
	95 min	0.83±0.04	0.82±0.04	0.80±0.05	0.81±0.03
Heart rate (beats/min)	15 min	109±12	115±12	114±10	114±12
	55 min	113±11	115±12	114±13	115±13
	95 min	115±11	118±13	115±18	118±12

* 95 min > 55 min. † 15 min > 95 min. ‡ Filtered air < all H_2SO_4 exposures.

§ 95 min < 55 min < 15 min.

sulfate exposure was a slightly lower respiratory frequency in the filtered air exposures than in the sulfate exposures. There were no significant alterations in heart rate.

Phase II

The metabolic variables measured during exposure under hot-humid conditions are summarized in Table 13. As anticipated, there were several pronounced changes due to heat exposure per se. There was a marked increase in heart rate and rectal temperature with successive exercise periods. There was also a slight rise in oxygen uptake over time. Ventilation increased slightly during the exposure, primarily as a result of a small increase in respiratory frequency. There was no effect of sulfate exposure on any of these variables.

TABLE 13. METABOLIC MEASUREMENTS DURING EXPOSURE TO FILTERED AIR AND SULFURIC ACID MIST (PHASE II, 0.9 μm PARTICLES, 35°C, 85% RH) (VALUES ARE MEANS ± STANDARD DEVIATION)

			H_2SO_4 Concentration ($\mu g/m^3$)		
	Time	Filtered Air	314	600	1107
Ventilation (ℓ/min BTPS)	15 min	33.5±5.8	33.0±4.1	31.8±3.4	33.7±5.2
	55 min	36.3±4.1	35.5±5.4	35.0±4.7	35.2±4.7
	95 min	36.1±6.2	37.2±6.7	36.9±5.9	36.2±4.7
Tidal volume (ml BTPS)	15 min	1571±511	1418±343	1597±385	1533±418
	55 min	1605±530	1521±543	1590±330	1517±393
	95 min	1479±448	1446±562	1621±436	1633±543
Respiratory frequency (breaths/min)	15 min	22.7±5.4	24.1±4.4	21.1±6.0	23.0±5.4
	55 min	24.2±6.0	25.2±6.4	22.7±4.7	24.0±6.2
	95 min	26.0±7.0	27.6±6.3	24.0±6.3	24.0±6.9
Oxygen uptake (ℓ/min STPD)	15 min	1.31±0.31	1.37±0.17	1.33±0.18	1.34±0.25
	55 min	1.38±0.24	1.41±0.26	1.36±0.18	1.35±0.26
	95 min	1.34±0.27	1.41±0.27	1.40±0.19	1.40±0.17

(CONTINUED ON NEXT PAGE)

TABLE 13 (continued)

	Time	Filtered Air	H_2SO_4 Concentration ($\mu g/m^3$) 223	600	1107
Respiratory exchange ratio	15 min	0.88±0.03	0.87±0.04	0.86±0.03	0.83±0.02
	55 min	0.84±0.04	0.86±0.04	0.87±0.06	0.86±0.04
	95 min	0.89±0.07	0.86±0.05	0.84±0.06	0.82±0.03
Heart rate (beats/min)	15 min	139±33	136±21	136±24	141±28
	55 min	155±33	153±18	149±18	157±26
	95 min	154±35	159±18	156±16	160±28
Rectal temperature (°C)	15 min	37.6±0.6	37.4±0.4	37.4±0.5	37.7±0.5
	55 min	38.1±0.6	38.0±0.6	38.1±0.4	38.3±0.6
	95 min	38.3±0.9	38.3±0.6	38.2±0.4	38.7±0.6

SECTION 7

DISCUSSION

It is abundantly clear from the results obtained in these two studies that sulfuric acid mist in the 1 μm particle size range and in concentrations up to 1200 $\mu g/m^3$ has relatively little effect on the cardiopulmonary system as determined by the non-invasive procedures which we employed.

We are unable to explain the significant decrease in forced vital capacity from pre- to post-exposure in 25°C conditions. We have previously observed a drop in FVC following exposure to filtered air under hot conditions (Folinsbee et al., 1977). There was no consistent pattern of response although there were a few significant changes that were related to sulfate exposure such as a decrease in $FEV_{1.0}$ on exposure to 939 $\mu g/m^3$ at 25°C, 55% RH. A small number of statistically significant observations are to be expected in a study of this nature on the basis of chance alone. The absence of any other supportive evidence suggests that the $FEV_{1.0}$ decrease of 100 ml is significant only by chance. Furthermore, subjects exposed to approximately 1400 $\mu g/m^3$ showed no alterations in pulmonary function.

Analysis of the metabolic data revealed a decrease in tidal volume (V_t) and an increase in respiratory frequency (f_R) during exposure to sulfate at 25°C, 55% RH. This observation is consistent with the findings of Amdur et al. (1952) but the magnitude of the change we observed is considerably smaller than the change they observed. A decrease in tidal volume and an increase in respiratory frequency is a typical response to respiratory irritants and may suggest some stimulation of irritant receptors as a result of sulfate exposure. The fact that the subjects could detect a "tickle" in their throat upon taking a deep breath supports this hypothesis. V_T and f_R were not altered during the exposure under hot-humid conditions. The tachypnea normally associated with hyperthermia may have masked such a change.

Sim and Pattle (1957) reported a more pronounced effect of a "wet" sulfuric acid mist than of a "dry" mist. There were no differences in the present study between the two conditions which differed dramatically in atmospheric water vapor content. However, we used a much lower concentration of sulfuric acid mist and maintained a constant particle size, whereas particle size increased in Sim and Pattle's study under the high-humidity condition.

Larson et al. (1977) have demonstrated that sulfuric acid mist of concentration 600 $\mu g/m^3$ is neutralized in the mouth. This process occurs relatively rapidly (0.2-1.0 s), but it is not clear what concentration of inspired sulfate aerosol is sufficient to saturate this mechanism. Calculations suggest that greater than 50% of sulfate aerosol at 600 $\mu g/m^3$ would be so neutralized. Clearly small particles would be neutralized more rapidly than large particles.

The absence of dramatic changes in lung function or respiratory pattern suggest that, at the concentrations to which our subjects were exposed, respiratory defense mechanisms such as ammonia neutralization or respiratory mucus may have been sufficient to protect the respiratory system from the effects of sulfuric acid.

REFERENCES

1. Air and Industrial Hygiene Laboratory of California, State Department of Health. Determination of sulfate in high volume particulate samples: Turbidimetric barium sulfate method. 1976. (Modified from Public Health Service Publication No. 999-AP-11, Selected Methods for the Measurement of Air Pollutants. "Determination of Sulfate in Atmospheric Suspended Particulates: Turbidimetric Barium Sulfate Methods." Cincinnati: U.S. Department of Health, Education, and Welfare, 1965.)

2. Amdur, M. O., L. Silverman, and P. Drinker. Inhalation of sulfuric acid mist by human subjects. Arch. Ind. Hyg. Occup. Med. 6: 305-313, 1952.

3. Anderson, T., J. Brown, J. Hall, and R. J. Shephard. The limitations of linear regressions for the prediction of vital capacity and forced expiratory volume. Respiration 25: 140-158, 1968.

4. Avol, E. L., M. P. Jones, R. M. Bailey, N. N. Chang, M. T. Kleinman, W. S. Linn, K. A. Bell, and J. D. Hackney. Controlled exposures of human volunteers to sulfate aerosols. Am. Rev. Respir. Dis. 120: 319-326, 1979.

5. Folinsbee, L. J., S. M. Horvath, P. B. Raven, J. F. Bedi, A. R. Morton, B. L. Drinkwater, N. W. Bolduan, and J. A. Gliner. Influence of exercise and heat stress on pulmonary function during ozone exposure. J. Appl. Physiol. 43: 409-413, 1977.

6. Kleinman, M. T., and J. D. Hackney. Effects of sulfate aerosols upon human pulmonary function. APRAE Project CAPM-27-75, Coordinating Research Council, Inc., New York, NY, 1978.

7. Larson, T. V., D. S. Covert, R. Frank, and R. J. Charlson. Ammonia in the human airways: Neutralization of inspired acid sulfate aerosols. Science 197: 161-163, 1977.

8. Lippmann, M., R. E. Albert, D. B. Yeats, K. Wales, and G. Leikauf. Effect of sulfuric acid mist on mucociliary bronchial clearance in healthy non-smoking humans. J. Aerosol Sci. In press, 1980.

9. Sackner, M. A., D. Ford, R. Fernandez, J. Cipley, D. Perez, M. Kwoka, M. Reinhart, E. D. Michaelson, R. Schreck, and A. Wanner. Effects of sulfuric acid aerosol on cardiopulmonary function of dogs, sheep and humans. Am. Rev. Respir. Dis. 118: 497-510, 1978.

10. Sim, Van M., and R. E. Pattle. Effect of possible smog irritants on human subjects. J. Am. Med. Assoc. 165: 1908-1913, 1957.

11. Swaroop, A. A micromethod for the determination of urinary inorganic sulfates. Clin. Chim. Acta 46: 333-336, 1973.

12. Walters, R. B. Generation and characterization of sulfuric acid aerosols for use in animal inhalation studies. M.S. Thesis, University of California, Irvine, CA 1976.

GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

(1) RESPIRATORY MEASUREMENTS

Parameter and Formula	Abbreviation	Units
1. Ventilatory Volume		
(a) $\dot{V}_E$ (uncorrected volume)	$\dot{V}_E$	ℓ/min
(b) $\dot{V}_E$ BTPS = $\dot{V}_E \times \frac{310}{273 + \text{gas temp.}} \times \frac{BP - WVP}{BP - 47}$	$\dot{V}_E$ BTPS	ℓ/min
(c) $\dot{V}_E$ STPD = $\dot{V}_E \times \frac{P_{bar} - P_w}{760} \times \frac{273}{273 + \text{gas temp.}}$	$\dot{V}_E$ STPD	ℓ/min
	P_{bar} = barometric pressure	
	P_w = water vapor pressure at the gas temperature	
2. Respiratory Rate	RR or f_R	breaths/min
3. Tidal Volume		
$\frac{\dot{V}_E}{RR}$	V_T	ml/breath

Parameter and Formula	Abbreviation	Units
4. (a) Ventilatory Equivalent Ratio (Oxygen)		
$\frac{\dot{V}_E \text{ BTPS}}{\text{Oxygen Uptake STPD}}$	$\dot{V}_E \text{ BTPS}/\dot{V}_{O_2}$	
(b) Ventilatory Equivalent Ratio (Carbon Dioxide)		
$\frac{\dot{V}_E \text{ BTPS}}{CO_2 \text{ Production (STPD)}}$	$\dot{V}_E \text{ BTPS}/\dot{V}_{O_2}$	

(2) METABOLIC MEASUREMENTS

1. Oxygen Uptake		
(a) $\frac{\dot{V}_E \text{ STPD} \times \text{True } O_2\%}{100}$	$\dot{V}_{O_2}$	$\ell\ O_2/\text{min}$
(b) $\frac{\dot{V}_E \text{ STPD} \times \text{True } O_2\% \times 1000}{100 \times \text{Pre Wt (kg)}}$	$\dot{V}_{O_2}$	$\text{ml } O_2/\text{kg}\cdot\text{min}^{-1}$
(c) $\frac{\dot{V}_E \text{ STPD} \times \text{True } O_2\% \times 1000}{100 \times \text{Lean Body Mass (kg)}}$	$\dot{V}_{O_2}$	$\text{ml } O_2/\text{LBM}\cdot\text{min}^{-1}$, LBM kg
2. True Oxygen		
$(\%N_2 \times 0.265) - \%O_2$ in expired air	True O_2	%
3. Respiratory Exchange Ratio	R	no units
$\frac{\%\text{ Expired } CO_2}{\%\text{ Expired } O_2}$ or $\frac{CO_2 \text{ Production}}{\text{Oxygen Uptake}}$	$\frac{\dot{V}_E\ CO_2}{\dot{V}_{O_2}}$	

Parameter and Formula	Abbreviation	Units
4. Excess Carbon Dioxide	Excess CO_2	ℓ
$\dot{V}_E$ STPD x $\frac{(\%CO_2 \text{ Expired} - 0.03)}{100}$ - $\dot{V}_{O_2}$ x 0.75		
5. Maximal Aerobic Power	$\dot{V}_{O_2\ max}$	ℓ/min
and/or		ml O_2/kg·min^{-1}
Maximal Aerobic Capacity		ml O_2/LBM·min^{-1}
(The largest value of oxygen uptake obtained when a subject performs maximal exhaustive work.)		
6. Percent of Maximal Oxygen Uptake	$\%\dot{V}_{O_2\ max}$	%
$\frac{\dot{V}_{O_2}}{\dot{V}_{O_2\ max}}$ x 100		
7. Energy Production		
cal/ℓ O_2 = 1.27604 x R + 3.82041		
(a) = cal/ℓ O_2 x 60 x ℓ O_2/min	M	kcal/h
(b) = $\frac{\text{kcal/h}}{\text{Pre Wt, in kg}}$	M	kcal/kg·h^{-1}
(c) = $\frac{\text{kcal/h}}{\text{BSA}}$	M	kcal/m^2·h^{-1}
(d) = kcal/m^2·h^{-1} x 1.163	M	W/m^2

Parameter and Formula	Abbreviation	Units
(3) CARDIOVASCULAR		
1. Cardiac Output = Stroke Volume x HR $\frac{\dot{V}_{O_2\ STPD}}{C_aO_2 - CO_2}$	$\dot{Q}$	ℓ/min
2. Cardiac Index $\frac{\dot{Q}}{BSA,\ in\ m^2}$	CI Body Surface Area = BSA	$\ell/min \cdot m^{-2}$
3. Cardiac Work $\frac{SP \times 13.6 \times \dot{Q}}{1000}$	CW	kg·m/min
4. Heart Rate	HR, f_C	beats/min
5. Stroke Volume $\frac{\dot{Q}}{HR}$	SV	ml/beat
6. Stroke Index $\frac{SV}{BSA}$	SI	$ml/beat \cdot m^{-2}$
7. Stroke Work $\frac{SP \times 13.6 \times SV}{1000}$	SW	g·m/beat

Parameter and Formula	Abbreviation	Units
8. Oxygen Pulse $\frac{\dot{V}_{O_2} \times 1000}{HR}$	O_2 Pulse	ml O_2/beat
9. Arteriovenous Oxygen Difference $\frac{\dot{V}_{O_2} \times 1000}{\dot{Q}}$	(a - v)O_2 diff.	ml O_2/ℓ blood
10. Systolic Pressure (Arterial)	SP, P_{syst}	torr
11. Diastolic Pressure (Arterial)	DP, P_{dias}	torr
12. Mean Blood Pressure (Arterial) $\frac{SP - DP}{3} + DP$	MPP, $\bar{P}_{bl}$	torr
13. Pulse Pressure $SP - DP$	PP	torr
14. Total Peripheral Resistance $\frac{1.333 \times 60 \times MBP}{\dot{Q}}$	TPR	dyn·s cm^{-5}

Parameter and Formula	Abbreviation	Units
(4) PULMONARY		
1. Forced Vital Capacity	FVC	(ml, ml/kg) ml/m^2
2. Timed Forced Expired Volumes (1.0, 2.0, and 3.0 seconds)	$FEV_{1.0}$	ml
	$FEV_{2.0}$	ml
	$FEV_{3.0}$	ml
3. Forced Expired Volumes as a percentage of Forced Vital Capacity	$FEV_{1.0}/\%FVC$	%
	$FEV_{2.0}/\%FVC$	%
	$FEV_{3.0}/\%FVC$	%
$\frac{FEV_{1.0}}{FVC} \times 100$		
4. Inspiratory Capacity	IC	ml
5. Expiratory Reserve Volume	ERV	ml
6. Functional Residual Capacity	FRC	ml
7. Residual Volume	RV	ml, ml/kg, ml/m^2
8. Total Lung Capacity	TLC	ml, ml/kg, ml/m^2
VC + RV		
9. Residual Volume/Percent Total Lung Capacity	RV/%TLC	%
$\frac{RV}{TLC} \times 100$		

Parameter and Formula	Abbreviation	Units
10. Maximal Mid-Expiratory Flow	MMEF	ℓ/s
or		
Mean Forced Expiratory Flow during middle half of FVC	FEF25-75%	
11. Maximal Voluntary Ventilation	MVV	ℓ/min
12. Maximal Expiratory Flow at 50% of Vital Capacity	MEF50%	ℓ/s
or		
Forced Expiratory Flow at 50% of FVC exhaled	FEF50%	
13. Maximal Expiratory Flow at 25% of Vital Capacity	MEF25%	ℓ/s
or		
Forced Expiratory Flow at 75% of FVC exhaled	FEF75%	
14. Closing Volume	CV	ml

(5) HEMATOLOGIC

1. Hemoglobin	Hb	mMoles/ℓ, g%
2. Hematocrit	Hct	%
3. Plasma Proteins		g%
4. Lactate	HLa	mEq/ℓ

Parameter and Formula	Abbreviation	Units
5. Carboxyhemoglobin	HbCO	%, vol%
$\frac{\text{HbCO (vol\%)}}{\text{Hb (g\%) x 1.39}} \times 100$		
(6) TEMPERATURE REGULATORY		
1. Rectal Temperature	T_{re}	^{o}C
2. Forehead Temperature	T_{hd}	^{o}C
3. Arm Temperature	T_{arm}	^{o}C
4. Finger Temperature	T_{fing}	^{o}C
5. Thigh Temperature	T_{thi}	^{o}C
6. Calf Temperature	T_{calf}	^{o}C
7. Chest Temperature	T_{ch}	^{o}C
8. Toe Temperature	T_{toe}	^{o}C
9. Room Temperature	T_{rm}	^{o}C
10. Ambient Air Temperature	T_{a}	^{o}C
11. Radiant Temperature	T_{r}	^{o}C
12. Black Globe Temperature	T_{g}	^{o}C
13. Wall Temperature	T_{wall}	^{o}C

Parameter and Formula	Abbreviation	Units
14. Wet Bulb Temperature	T_{wb}	^{o}C
15. Mean Skin Temperature	$\bar{T}_{sk}$	^{o}C

$$\bar{T}_{sk} = 0.07\ T_{head} + 0.36\ T_{chest} + 0.05\ T_{finger} + 0.14\ T_{arm} + 0.05\ T_{toe} + 0.13\ T_{calf} + 0.20\ T_{thigh}$$

16. Mean Body Temperature — $\bar{T}_b$ — ^{o}C

$$0.65\ T_{re} + 0.35\ \bar{T}_{sk}$$

17. Body Heat Content — BHC — $kcal/m^2$

$$\frac{\text{Pre Wt (kg)} \times 0.83\ \bar{T}_b}{\text{BSA}}$$

18. Wet Bulb Globe Temperature Index — WBGT — ^{o}C (^{o}F)

$$0.3\ T_g + 0.7\ T_{wb}$$

19. Tissue Conductance — K — $kcal/m^2 \cdot h^{-1} \cdot {}^{o}C^{-1}$

$$\frac{kcal/m^2 \cdot h^{-1}}{T_{re} - \bar{T}_{sk}} = \frac{\text{Energy Prod.}}{T_{re} - \bar{T}_{sk}}$$

20. Respiratory Evaporative Water Loss — Resp. H_2O Loss — g/h

$\dot{V}_E$ BTPS x factor x 60

(The factor is determined from density steam tables and is dependent on temp. of expired gases.)

Parameter and Formula	Abbreviation	Units
21. Respiratory Evaporative Heat Loss	Resp. Heat Loss ($-E_r$)	$kcal/m^2 \cdot h^{-1}$

$$\frac{\text{Resp. } H_2O \text{ Loss} \times 0.58}{\text{BSA}}$$

22. Skin Evaporative Heat Loss	Evap. Heat Loss ($-E_{sk}$)	$kcal/m^2 \cdot h^{-1}$

$$\frac{(\text{Pre Wt} - \text{Post Wt} - \text{Resp. } H_2O \text{ Loss} - \text{Excess } CO_2 \text{ (g)}) \times 0.580}{\text{BSA}}$$

ALPHABETICAL LIST OF ABBREVIATIONS AND SYMBOLS

$(a - v)O_2$ diff.	arteriovenous oxygen difference
alveol. (A)	alveolar
AQS	air quality standards
bar.	barometric
BHC	body heat content
BMR	basal metabolic rate
BP	blood pressure
BSA	body surface area
BTPS	body temperature and pressure, saturated with water vapor
cal	calorie(s)
C_aO_2	arterial oxygen content
cfm	cubic feet per minute
CI	cardiac index
cm	centimeter(s)
CNS	central nervous system
CO	carbon monoxide
CO_2	carbon dioxide
CV	closing volume
C_VO_2	venous oxygen content
CW	cardiac work
^oC	degree(s) Celsius
^oF	degree(s) Fahrenheit
dias.	diastolic
diff.	difference
diff. perf.	diffusion perfusion

$D_{L_{CO}}$	diffusion capacity to carbon monoxide
DP	diastolic pressure
dyn	dyne(s)
$-E_r$	respiratory evaporative heat loss
$-E_{sk}$	skin evaporative heat loss
ECG	electrocardiogram, electrocardiograph
EPA	Environmental Protection Agency
ERV	expiratory reserve volume
evap.	evaporative
FA	filtered air
f_C	cardiac frequency (same as HR)
FEF50%	forced expiratory flow after 50% of FVC exhaled
FEF75%	forced expiratory flow after 75% of FVC exhaled
FEF25-75%	forced expiratory flow during middle half of FVC
ΔFEF75%	difference between FEF75% on helium and air flow volume curve
FEV	forced expired volume
$FEV_{1.0}$	forced expired volume (1.0 second)
$FEV_{2.0}$	forced expired volume (2.0 seconds)
$FEV_{3.0}$	forced expired volume (3.0 seconds)
f_R	respiratory frequency
FRC	functional residual capacity
FVC	forced vital capacity
g	gram(s)
h	hour(s)
Hb	hemoglobin

HbCO	carboxyhemoglobin
Hct	hemocrit
HLa	lactate
H_2O	water
H_2SO_4	sulfuric acid
HNO_2	nitrous acid
HNO_3	nitric acid
HR	heart rate (same as f_C)
ht	height
IC	inspiratory capacity
K	tissue conductance
kg	kilogram(s)
KI	potassium iodide
LBM	lean body mass
ℓ	liter(s)
m	meter(s)
m^3	cubic meters
M	energy production
max	maximal
MBP	mean blood pressure
MEF	maximal expiratory flow
MEF25%	maximal expiratory flow at 25% of vital capacity
MEF50%	maximal expiratory flow at 50% of vital capacity
MEF25-75%	maximal expiratory flow at 25-75% of vital capacity (same as MMEF)

mEq	milliequivalent(s)
min	minute(s)
ml	milliliter(s)
MMEF	maximal mid-expiratory flow (same as MEF25-75%)
mMoles	millimoles
MVV	maximal voluntary ventilation
N_2	nitrogen
N_2O_5	dinitrogen pentoxide
NaCl	sodium chloride
NO_2	nitrogen dioxide
NO_x	oxides of nitrogen
nom.	nominal
NRC	National Research Council
O_2	oxygen
O_3	ozone
P	probability of wrongfully rejecting the null hypothesis (level of significance)
P_aO_2	arterial pressure of oxygen
P_AO_2	alveolar pressure of oxygen
P_{bar}	barometric pressure
$\bar{P}_{bl}$	mean blood pressure
$P_{dias.}$	diastolic pressure
P_{O_2}	partial pressure of oxygen
$P_{syst.}$	systolic pressure
P_w	water vapor pressure
$P_v\text{-}CO_2$	mixed venous carbon dioxide partial pressure

PAN	peroxyacetylnitrate
%	percent
perf.	perfusion
PIF	point of identical flow on helium and air flow volume curves
PP	pulse pressure
ppm	parts per million
press.	pressure
prod.	production
$\dot{Q}$	cardiac output
R	respiratory exchange ratio
R_{aw}	airway resistance
RBC	red blood cell
resp.	respiratory
rh	relative humidity
RR	respiratory rate (same as f_R)
R-R	electrocardiograph interval from point R to point R
RV	residual volume
s	second(s)
SD	standard deviation
SE	standard error
SI	stroke index
SO_x	sulfur oxides
SP	systolic pressure
STPD	standard temperature and pressure, dry
SV	stroke volume
SVC	slow vital capacity

SW	stroke work
syst.	systolic
T_a	ambient air temperature
T_{arm}	arm temperature
$\overline{T}_b$	mean body temperature
T_{calf}	calf temperature
T_{ch}	chest temperature
T_{fing}	finger temperature
T_g	black globe temperature
T_{hd}	forehead temperature
T_r	radiant temperature
T_{re}	rectal temperature
T_{rm}	room temperature
$\overline{T}_{sk}$	mean skin temperature
T_{thi}	thigh temperature
T_{toe}	toe temperature
T_{wall}	wall temperature
T_{wb}	wet bulb temperature
temp.	temperature
TGV	thoracic gas volume
TIS	Technical Information Staff (EPA)
TLC	total lung capacity
TLV	threshold limit values
torr	unit of pressure
TPR	total peripheral resistance
V	volume

$\dot{V}$	timed ventilatory volume
$\dot{V}_A$	alveolar ventilation
$\dot{V}_A/\dot{Q}$	ventilation perfusion ratio
$\dot{V}_E$	ventilatory volume, expired
$\dot{V}$max50% VC	instantaneous forced expiratory flow when lung is at 50% of its forced vital capacity (same as FEF50%)
$\dot{V}$max75% VC	instantaneous forced expiratory flow when lung is at 75% of its forced vital capacity (same as FEF75%)
$\dot{V}_{O_2}$	oxygen uptake
$\dot{V}_{O_2\ max}$	maximal aerobic capacity (maximal aerobic power)
V_T	tidal volume
VC	vital capacity
W	watt(s)
WBGT	wet bulb globe temperature index
WVP	water vapor pressure
wt	weight
yr	year(s)
χ^2	statistical datum derived in the chi-square test

APPENDIX.

DETERMINATION OF SULFATE: TURBIDOMETRIC BARIUM SULFATE METHOD

DETERMINATION OF SULFATE: TURBIDOMETRIC BARIUM SULFATE METHOD

Reference: AIHL (Air and Industrial Hygiene Laboratory) Method #61, Revised July 1976.

Introduction: The AIHL Method No. 61 as revised July 1976: Determination of Sulfate in High Volume Particulate Samples: Turbidometric Barium Sulfate Method (Attachment 1 to this IES Method) is followed insofar as practicable with regard to available equipment and experimental designs. The details of the method as applied in this laboratory are given below.

Principle: A water extract of the filter sample is treated with barium chloride to form a barium sulfate colloidal suspension. The turbidity of the suspension is measured nephelometrically at 500 nm.

Glassware: All glassware is washed with detergent, rinsed in tap and demineralized water (in an automatic washer) and dried. It is then soaked a minimum of 20 minutes in 15-20% nitric acid and rinsed in glass distilled water and dried. A rinse with reagent grade alcohol or acetone may be used for quicker drying.

Reagents: All reagents are made with distilled-deionized water. Only analytical reagent grade (ACS) chemicals are used.

1. Hydrochloric acid, 10N

Water	20 ml
HCl	80 ml

   Carefully add acid to water in a 100-ml glass-stoppered graduated cylinder. Dilute to mark with water. USE HOOD. Do not breathe acid vapor!

2. Glycerol - alcohol - acid solution.

Glycerol	20 ml
95% ethyl alcohol	40 ml
10N HCl	15 ml

   Mix well. Store in glass-stoppered Erlenmeyer flask.

3. Barium chloride. $BaCl_2.2H_2O$ crystals, 20-30 mesh. J.T. Baker Catalog #0974 or equivalent.

   Weigh out 0.025-0.026 mgm aliquots and place in small glass tubes (6 x 50 mm). Keep covered.

4. Standard sulfate solution (100 µgm sulfate/ml). Dry anhydrous sodium sulfate at 105°C for at least 4 hours. Cool in a desiccator using silica gel as a desiccant. DO NOT USE DRIERITE.

   Weigh 0.148 gm and dissolve in water to make 1 liter.

   F.W. Na_2SO_4 = 142.04 $SO_4^=$ wt = 96.02

   $$\cancel{1000} \times \frac{1}{\cancel{1000}} \times \frac{148}{142} \times 96 = 100 \ (\mu gm/ml)$$

Filters: Gelman AE glass fiber filters are soaked in 20% HNO_3 for 30 minutes. They are then rinsed five times each side using a Buchner funnel with 20% HNO_3. The acid rinse is followed by five rinses with double-distilled water. The filters are then soaked in double-distilled water and rerinsed. The final rinse is with isopropyl alcohol (80%) to facilitate drying. The filters are dried in the oven at about 104°F (40°C).

Sample Collection: All glassware and utensils are washed in 20% HNO_3 and rinsed with double-distilled water.

Filters are loaded into Gelman 47mm open-face or in-line filter holders (model 1220, 1235) using clean forceps. The filter holders are inserted into a plexiglass tube which in turn is inserted through the chamber wall. The filter protrudes beyond the end of the plexiglass tube and is located directly above the chamber exit port. The tube fitting of the filter holder is connected to a Sierra Instruments sample pump which samples at 25-30 l/min. Sampling is normally performed for 15-30 min; timing is automatic. Aliquoting is adjusted so that samples containing 2-60 µg/ml sulfate can be assayed.

Filters are unloaded and placed in a nitric acid washed 12-ml glass-stoppered centrifuge tube containing 6 ml of double-distilled water. After soaking, the filter is macerated with a nitric acid washed stainless-steel spatula and the tube is centrifuged for 20 min @ 2100 rpm (1000 g). The supernatant is used for assay.

Method: Pipet 2 ml of supernatant into a 1-cm ground-glass-stoppered fluorometer cuvette. Add 0.5 ml glycerol - acid - alcohol solution using an eppendorf pipet. Mix.

Blank reading:

Set both monochromators of Farrand spectrofluorometer to 500 nm.
Set zero with shutter closed.
Adjust "gain" control so that the "L4" lucite block (see Technical Note section) reads 90 on the meter.
Take a blank reading for each cuvette.
Read the lucite block (but do not readjust gain control) after every three or four blank readings.

Add 0.025 gm barium chloride crystals. Shake vigorously for 20 seconds. Add the barium chloride crystals to the remaining cuvettes at 30-second intervals. Shake all cuvettes again for 20 seconds. Let stand at room temperature (20-30°C) for 40 minutes.

Each batch of samples MUST include a blank (2 ml double-distilled water instead of supernatant) and three standards, usually 10, 20, and 30 µgm/ml or 20, 30, and 40 µgm/ml depending upon the expected range (use 2 ml of standard solution for assay).

If high values are expected, 1-ml aliquots of unknowns and standards (40, 50, and 60 µgm/ml) are used plus 1 ml of double-distilled water added with an Eppendorf pipet.

Mix gently and read against the "L4" lucite block set at 90.0 as before.

Calculations:

A. Sulfate Concentration of Filter Extract

Calculate the mean reading of the "L4" lucite block for each set of readings.

Scale all readings as follows:

$$\frac{100}{\bar{X} \text{ rdg lucite block}} \times \text{test reading} = \text{scaled value.}$$

Subtract the scaled blank from the scaled test readings to get "corrected" reading.

Calculate the linear regression coefficients.

Conc. Unknown = a + b ("corrected" reading).

Record the slope, intercept, correlation coefficient, and standard error.

B. Sulfate Concentration in Chamber

a) The air flow passing through the filter is automatically adjusted for increasing filter resistance and is calibrated by volume displacement for conditions of 760 torr and 22°C.

b) The chamber concentration is then calculated as $\mu g/m^3$ using the following equation:

$$\mu g/m^3 = \frac{\mu g/ml \times A}{0.001 \times flow \times time}$$

where A = total volume of filtrate in mils
flow = flow in liters/min
time = sample time in minutes

Technical Note: The use of a lucite reference for fluorometry and nephelometry was introduced to this laboratory by Ms. Helen Campuzano.

The lucite is cut to the size and shape of a 1-cm cuvette and polished on all sides. It should fit securely into the cuvette holder. It is then lightly scratched with fine sandpaper until it can be set to an arbitrary value (usually 80-100%) in the desired range. The top of the block is marked so that it can always be inserted in the same direction relative to the light path.

By adjusting the fluorometer with the reference block, test readings can be scaled and the readings of standards, etc. can be compared from day to day since the readings are all relative to the same reference point. It also allows off-scale test readings to be brought on scale by gain control adjustments because the lucite block can be read at this new setting. The true test reading can be readily calculated.

By taking readings of the lucite block at intervals during test readings, the operator is made instantly aware of any difference in instrument operation such as drift or a change in sensitivity.

Error Analysis: Standard preparation and assay excluding nephelometer error. (Barium sulfate method.)

Analytical balance	±0.02%
1-liter volumetric flask, class A	±0.03%
10-ml volumetric flask, class A	±0.20%
1-ml volumetric pipet, class A	±0.60%
2-ml volumetric pipet, class A	±0.30%
0.5-ml Eppendorf pipet	±1.00%

Standard deviation $= \sqrt{\Sigma\sigma^2}$ = ±1.2% for 10 µgm SO_4/ml standard.

Error is slightly less for higher concentrations of standard because the error of the larger class A volumetric pipet is smaller.

Linear regression, correlation coefficient and standard error of the estimate for all standards and blanks run between 25 February 1980 and 10 April 1980 is given below. There were 14 batches which were run with 1-ml aliquots of standards and test samples. Calculations were made from 104 readings (against lucite reference block) on 52 standards and blanks (0, 40, 50, and 60 µgm SO_4/ml).

N = 104 readings on 52 samples
intercept = -0.15 scale division
slope = 0.73 µgm SO_4 per scale division
correlation coefficient = 0.998
standard error = 1.37

The mean percent error calculated from 71 duplicate assays done in separate batches on different days, and in most cases by different technicians, was within 5% (4.8%). The concentration range was from 2 to 68 μgm SO_4/ml (mean = 31 μgm SO_4/ml).

Collection Filters: Glass fiber filters (Gelman Type AE) were selected for filter collection of sulfate on the basis of 99.9% efficiency of 0.3-μ aerosol particles and the ability to treat these filters to remove inherent sulfate composition and interfering ion or metal contaminants. Although other filter types have been recommended by various manufacturers, either pore size (usually greater than 1 micron) or working material have eliminated these filters from consideration. Table 1 lists the physical/chemical properties of the Gelman Type A/E filters as stated by the manufacturer.

The Gelman filters are composed of low acid soluble glass fibers. Treatment of the filters prior to use was found necessary as the filters contain some sulfate and interfering ions (Table 2). Filters were treated by washing with nitric acid and multiple water washings followed by drying.

Results of initial testing of washed and unwashed filters using the Swaroop micromethod for the determination of inorganic sulfates is shown in Table 2. The negative values indicate the presence of substances other than sulfate which interfere with the color reaction. Table 3 shows the recovery efficiency of known standards. Acid-washed filters were prepared for recovery tests by loading with potassium sulfate solutions. Analysis was performed by an independent technician again using the Swaroop method.

TABLE 1. TYPE A/E GLASS FIBER FILTERS*

The following physical/chemical properties represent typical, average values obtained in accordance with accepted test methods. They are subject to normal manufacturing variations and are supplied as a technical service. The analysis has been made in accordance with EPA procedures (micrograms/ 8- x 10-inch sheet).

ELEMENTS:

Antimony	20
Arsenic	20
Beryllium	1
Bismuth	10
Cadmium	2
Chromium	10
Cobalt	10
Copper	2
Iron	100-1800
Lead	10
Manganese	2
Mercury	80
Molybdenum	10
Nickel	10
Selenium	200
Tin	10
Titanium	10
Vanadium	10
Zinc	90

WATER EXTRACTABLE IONS:

Sulfate	600
Nitrate	115
Ammonia	13
Chloride	1500
Fluoride	87

* Courtesy of Gelman Instrument Co.

TABLE 2. SULFATE (μg/ml) ANALYSIS ON FILTERS

(Swaroop Method)

Filter	Untreated	HNO_3 Treated
No. 1	-12.5	1.6
No. 2	- 8.2	0.0
No. 3	- 4.6	0.9
No. 4	- 4.0	0.4

TABLE 3. RECOVERY EFFICIENCY OF KNOWN STANDARDS

(Swaroop Method)

	HNO_3 Treated		
1.	94.5	6.	99.0
2.	97.7	7.	93.0
3.	99.1	8.	101.0
4.	99.0	9.	100.0
5.	91.1	10.	99.1

Mean 97.4

DETERMINATION OF SULFATE IN HIGH VOLUME PARTICULATE SAMPLES: TURBIDIMETRIC BARIUM SULFATE METHOD*

Analyte:	Sulfate	Method No.	61
Application:	Air Pollution	Range:	2 to 40 µg sulfate/m^3
Matrix:	Air	Lower Detection Limit:	50 µg sulfate/ 20 ml solution
Procedure:	Collection on filter by high-volume sampler, extraction with water followed by turbidimetric analysis	Precision:	5 to 11% coefficient of variation

Date First Issued: December, 1974

Dates Revised: April, 1975; February, 1976; and July 1976

1. Principle of the Method

1.1 Atmospheric suspended particulate matter is collected over a 24-hour period on a 20 by 25 cm (8 by 10 inch) glass fiber filter by using a high-volume sampler. This method can also be used for samples collected on cellulose filters.

1.2 A water extract of the filter sample is treated with barium choloride to form a barium sulfate colloidal suspension. The turbidity of the suspension is measured spectrophotometrically at 500 nm.

1.3 The water extract can also be used for analysis of other water soluble species, e.g., NO_3^-, Cl^-, Na^+, NH_4^+.

*AIHL modification of Public Health Service Method (cf. Sec. 10.1). *Italicized sentences are changed from the February, 1976 revision of Method 61.* Prepared by staff of the Air and Industrial Hygiene Laboratory, State Department of Health, Berkeley, California.

2. Range and Lower Detection Limit

2.1 Aliquoting is adjusted so that samples containing 2 to 40 µg sulfate/m^3 (the expected range of atmospheric samples) can be measured.

2.2 The lower detectable concentration of the trubidimetric analytical procedure is 50 µg of sulfate in 20 ml solution.

3. Interferences

3.1 Measurement is dependent upon the stability of the suspension of colloidal barium sulfate particles, size of particles, sulfate concentration, barium ion strength, pH and temperature. These parameters must be closely controlled to avoid obtaining low and inconsistent results. Addition of glycerol acts as a stabilizer for the colloid, while alcohol promotes precipitation by reducing the solubility of barium sulfate. Use of solid crystals of $BaCl_2$ eliminates the problem of barium ion strength and solution aging. Sulfate concentration is maintained within the limits of the method, and pH is controlled by addition of dilute HCl. Variations in temperature between 20 and 30°C do not appear to have a significant effect. Vigorous shaking of the solution during the addition of barium chloride promotes the formation of finer particles that stay in suspension longer.

3.2 Sulfur-containing anions are generally strong positive interferents probably due to air oxidation of sulfate. Colloidal clay interferes strongly but in a direction apparently dependent on the sulfate/interferent ratio. Table 1 summarizes results of a recent AIHL study (cf. Sec. 10.2).

3.3 Glass fiber filters are not sulfate free. The amount of sulfate depends on the manufacturer's filter types and lots. For example, the MSA Type 1106 filters have been found to contain up to 4 mg sulfate per 20 by 25 cm sheet. This sulfate can be removed by water wash prior to sampling if desired. When this is not practical, as is the case for many monitoring purposes, determine the background sulfate concentration (section 7.3.6) for every lot and type of sampling filter used and correct the results accordingly.

3.4 Frequently the aqueous extract containing the sulfate shows background coloration and/or turbidity which may interfere with the analysis. These interferences are accounted for by measuring the absorbance (A_1) of the filtrate and glycerol-alcohol-acid mixture before the addition of the barium chloride. *This value is subtracted from the absorbance (A_2) of the samples after the addition of barium chloride.*

4. Precision and Accuracy

4.1 The precision of the method was established at AIHL by three determinations on each of the extracts from 12 high-volume atmospheric samples (cf. Sec. 10.2). Extracts were diluted into the optimal concentration range of the method. Under carefully controlled conditions, a coeffeicient of variation of 5% was found. This compares to the value of 5% given in ASTM method D516 (cf. Sec. 10.3) and to the value of 11% reported in the Public Health Service method (cf. Sec. 10.1).

4.2 *The extraction efficiency of the analytical method was recently evaluated at AIHL utilizing exhaustive extraction of ten 24-hour samples collected in Southern California. The mean recovery was 96.1 ± 1.2%.* Also MSA 1106 BH and Staplex TFA 810 filters were spiked with known amounts of sulfate salts and recoveries close to 100% were established.

5. Equipment

5.1 High-volume sampler. A motor blower filtration system with a sampling head which can accommodate a 20 by 25 cm glass fiber filter and capable of sampling at an initial flow rate of about 1.7 m^3/min (60 ft^3/min).

5.2 Filters. Use 20 by 25 cm (8 by 10 inch) glass fiber filters of low sulfate content.

5.3 Refluxing Apparatus. Use 125 ml flask with ground glass joint, a reflux condenser and a hot plate.

5.4 Filtering Funnel and Whatman No. 42 filter paper.

5.5 Cuvettes. Matched 20 mm or 1 inch cuvettes.

5.6 Pipettes. Use 20, 5 ml and other sizes as required.

5.7 Spectrophotometer. Capable of measuring at 500 nm *with a bandpass of 16 nm or less.*

5.8 Filtrate Receivers. 100 ml glass-stoppered graduated cylinders.

6. Reagents

All reagents should be made from ACS analytical-grade chemicals.

6.1 Hydrochloric acid (10 N). Add carefully 80 ml of concentrated hydrochloric acid to 20 ml of distilled water in 100 ml glass stoppered graduated cylinder and dilute to mark with water.

6.2 Glycerol-alcohol-acid solution. Mix 20 ml of glycerol with 40 ml of *reagent grade* 95% ethyl alcohol and 15 ml of 10.N HCl. *Caution: Do not use denatured alcohol.*

6.3 Barium chloride. $BaCl_2$ - 2 H_2O Crystals, 20-30 mesh. J. T. Baker Cat. No. 0974 or equivalent.

6.4 Standard sulfate solution (100 µg sulfate/ml). Dry anhydrous sodium sulfate at 105°C for 4 hours and cool in a desiccator. Dissolve 0.148 g of the dried anhydrous sodium sulfate in distilled water and dilute to 1 liter. This solution contains 100 µg sulfate per ml.

7. Procedure

7.1 Sampling. Using the high-volume sampler, collect the particulate matter from approximately 2000 m^3 of air. 24 hours is the usual sampling period. Note and record the airflow rates at the start and end of the sampling period.

7.2 Sample preparation. The sample filter should be delivered to the laboratory unfolded in a glassine envelope. *An aliquot of the filter is taken for analysis. (Appendix 1 discusses sectioning the filter for various analyses.) One-fourth of the filter (Quadrant A as shown in Appendix 1)* is cut into about 5 cm lengths for ease in handling and placed into the 125 ml boiling flask containing 50 ml of distilled water. *The sample is refluxed for 60 minutes.* The hot solution is filtered through a Whatman No. 42 filter paper which has been previously rinsed free of sulfate with at least 50 ml of boiling distilled water. The filtrate is collected in a 100 ml glass-stoppered graduated cylinder. Both the boiling flask and sample filter are rinsed 3 times with about 10 ml each of boiling distilled water. After cooling, the final filtrate

volume is brought up to 100 ml with distilled water.

7.3 Analytical Procedure

7.3.1 Pipette an aliquot of the filtrate, normally 20 ml, containing 50 to 1000 µg sulfate into a clean dry 25 ml glass-stoppered graduated cylinder. When a smaller aliquot is used, dulute to 20 ml with distilled water. Add 5 ml of the glycerol-alcohol-acid solution and mix.

7.3.2 Pour a portion of the solution in a dry cuvette. Determine the absorbance at 500 nm against distilled water and record as A_1.

7.3.3 Pour the sample solution in the sample cuvette back in the cylinder. Add approximately 0.25 g of barium chloride crystals, stopper the flask and shake it vigorously for 45 sec to dissolve the crystals.

7.3.4 Let the sample stand for exactly 40 min at room temperature (20 to 30°C). Then gently mix the suspension by inverting the graduated cylinder once and measure the absorbance (A_2) of the solution against distilled water as above. When large number of samples are to be analyzed, add the $BaCl_2$ crystals at timed intervals (e.g., 1 min) with similar intervals between spectrophotometer readings.

7.3.5 Analyze a standard sulfate soltuion as a control with each bach of samples to detect gross variations in the analysis. Deviations up to 5% from the standard curve are acceptable.

7.3.6 A correction for the background concentration of sulfate in the filters must be made for each new lot of filters. This value (B) must be the average of at least 5 determinations using 5 filters from each lot of 100 filters using the entire analytical procedure (Sec. 7.2 and 7.3) and must be subtracted as filter blank (Sec. 9.2).

8. Standards and Calibration

8.1 Prepare standard from the 100 µg sulfate/ml standard solution by pipetting respectively 0, 0.5, 1.0, 2.0, 3.0, 4.0, 6.0,

8.0, and 10.0 ml into 25 ml glass-stoppered graduated cylinders. Bring the volumes to 20 ml with distilled water. Analyze the standard solutions as in Sec. 7.3, but the determination of A_1 is unnecessary since negligible values are always obtained.

8.2 Plot the absorbance readings (A_2) on the vertical axis versus the corresponding µg of sulfate on the horizontal axis using rectilinear graph paper.

8.3 The relation between absorbance and amount of sulfate should be linear between 300 and 1000 µg. The slope of the curve in this range is calculated by least squares and used in determining the amount of sulfate in each sample. Below 300 µg, the relationship is non-linear and the sulfate concentration must be determined graphically.

9. Calculations

9.1 Air volume calculations

9.1.1 *For samples collected at altitudes less than 2000 ft above mean sea level, use the calibrated air flow rate, which is approximately equal to the flow rate under standard conditions of 760 Torr and 25°C.*

9.1.2 *For samples collected at altitudes of 2000 ft or greater, calibrate the high-volume sampler using the ARB procedure (4) which corrects the flow rate to standard sea level conditions.*

9.1.3 *Using the flow rate determined in 9.1.1 or 9.1.2 above, calculate the air volume from the sampling time and the average of the airflow rates at the start and end of the sampling period.*

$$V = \frac{(Q_1 + Q_2)}{2} t$$

Where: Q_1 = airflow rate at start of sampling period (m^3/min) *($ft^3/min \times 0.02832 = m^3/min$)*

Q_2 = airflow at end of sampling period

t = sampling period

V = sample volume in m^3 at standard conditions

9.2 Subtract A_1 from A_2 and, calculating from the calibration curve obtained in section 8, determine the equivalent µg of sulfate *(C) in the aliquot.* Calculate the concentration of sulfate in the 20 by 25 cm filter sample in $\mu g/m^3$ as follows:

$$\mu g \text{ sulfate}/m^3 = \frac{(F_1)(F_2)(C) - B}{V}$$

Where: $F_1 = \frac{\text{total ml of filtrate}}{\text{ml of filtrate taken for analysis}}$

$F_2 = \frac{\text{total sample area of filter sample}}{\text{sample area of filter quadrant analyzed}}$

C = µg sulfate in aliquot of sample taken

B = µg sulfate/20 x 25 cm filter blank

V = air sample volume in m^3 *(determined as in Sec. 9.1).*

10: References

10.1 Public Health Service Publication No. 999-AP-11, Selected Methods for the Measurement of Air Pollutants; "Determination of Sulfate in Atmospheric Suspended Particulates: Turbidimetric Barium Sulfate Method", pp. I-1, US Dept. of Health, Education and Welfare, PHS, Div. of Air Pollution, Robert A. Taft Sanitary Engineering Center, Cincinnati, OH 45226, May 1965.

10.2 Final Report, EPA Contract No. EPA 68-02-1660, "Comparison of Wet Chemical and Instrumental Methods for Measuring Airborne Sulfate", B. R. Appel, E. L. Kothny, E. M. Hoffer, and J. J. Wesolowski, February 1976.

10.3 ASTM Method D516-68 (Method B), "Standard Methods of Test for Sulfate Ion in Water and Waste Water"; 1975 Book of ASTM Standards; Part 31, Water; ASTM, Philadelphia, PA.

4. *Standard Procedure for the Calibration of Hi-Vol Samplers and Plotting of Flow Calibration Curves Corrected for Altitude, California Air Resources Board, September, 1975, Sacramento, CA.*

APPENDIX A

CUTTING OF GLASS-FIBER HIGH-VOLUME FILTERS

---

1. *Remove the glass-fiber filter from the shipping envelope.*

2. *Using a clean cutting tool, preferably stainsless steel, cut the filter in half. Then cut one half into two equal quadrants as shown in Figure 1.*

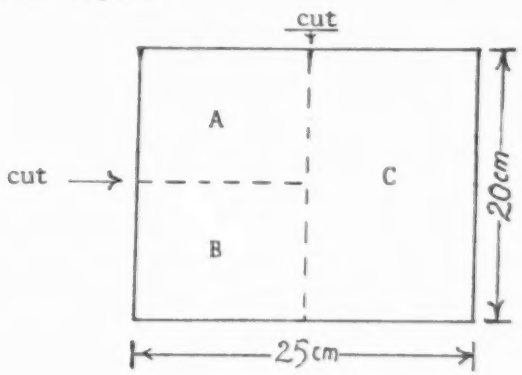


Figure 1.

3. *Use quadrant "A" for the determination of sulfate (AIHL Method 61) and nitrate (AIHL Method 66).*

4. *Use quadrant "B" for the determination of lead (AIHL Method 54).*

5. *Use half "C" for the determination of benzene-soluble organics (AIHL Method 67).*

TABLE 1.

THE EFFECT OF POTENTIAL INTERFERENTS IN THE $BaCl_2$ TURBIDIMETRIC METHOD[a]

Interferent	Sulfate/Interferent Ratio[b] 2:1 (w/w)	0.66:1 (w/w)
Sulfide	++	++
Sulfite	++	++
Persulfate	0	++
Thiosulfate	++	++
Bicarbonate	+	0
Phosphate	0	0
Silicate	0	0
Calcium	0	0
Lead	+	0
Colloidal Clay	-	++
P-Benzoquinone (a yellow chromophore used to simulate a yellow extract)	0	0

[a](+) indicates > 10% increase in sulfate
(++) indicates > 25% increase in sulfate
(0) indicates < 10% change in sulfate
(-) indicates > 25% decrease in sulfate

[b]sulfate concentration 20 µg/ml

Source: Ref. 10.2.

METHOD 61. TURBIDIMETRIC SULFATE - ADDENDUM

1. Limit of Detection

The method specifies that the lower detection limit is 50 µg per aliquot. This corresponds to a net absorbance of 0.03, i.e., $A_2 - A_1$. Since A_1 may be as large as 0.07, the chemist and section leader should carefully examine any A_2 value smaller than 0.10 absorbance units, with the thought that the net absorbance may be less than the limit of detection. In any case, all $A_2 - A_1$ values of 0.03 units or less should be considered as being less than 50 µg sulfate.

2. Range of the Method

The range of the method is given as 2 to 40 $\mu g/m^3$, equivalent to 200 to 4000 µg per aliquot. Actually, the curve is linear between 300 and 1500 µg sulfate, corresponding to absorbances from 0.10 to 0.90. (Note that the standards described in Method 61 do not cover this range. It should be modified to include 1200 and 1400 µg standards.) The optimum reading, from an instrumental standpoint, is 0.40 absorbance units. The following protocol should be adopted:

a. Aliquots shall be adjusted to an A_2 value of 0.40. Samples giving A_2 values less than 0.10 or greater than 0.90 must be rerun, using an appropriate aliquot size.

b. Standards greater than 1500 µg shall not be run, since they adversely affect the linear regression line.

c. Chemists shall not record, as a reportable result, $A_2 - A_1$ values greater than 0.90 nor less than 0.10, unless in the latter case, a 20 ml aliquot was used.

3. Analytical Procedure

There should be no deviation from the written procedure. If circumstances should require the section leader to temporarily modify the procedure, he should instruct the chemist to flag these

results and should, by memo, explain the circumstances to his group leader, the QA chairman, and the data handling section.

This memo should be attached to, and become a part of, the chemist's and sections leader's copies of Method 61.